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**What's in the sandwich? New P-T constraints for the (U)HP nappe stack of southern Dora-Maira Massif (Western Alps)**

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## What's in the sandwich? New P-T constraints for the (U)HP nappe stack of southern Dora-Maira Massif (Western Alps) --Manuscript Draft--

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<b>Full Title:</b>	What's in the sandwich? New P-T constraints for the (U)HP nappe stack of southern Dora-Maira Massif (Western Alps)
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<b>Abstract:</b>	<p>The Brossasco-Isasca Unit (BIU) of the southern Dora-Maira Massif (DMM), Western Alps, is one of the most studied ultra-high pressure (UHP) units in the world. However, the interpretation of UHP metamorphism in the BIU is still a highly debated and challenging issue. The structural and tectonometamorphic setting of the southern DMM is described in the literature as a tectonic "sandwich", with the UHP unit in the middle, bounded by two high-pressure (HP) eclogitic units in the footwall (the San Chiaffredo Unit, SCU) and hanging wall (the Rocca Solei Unit, RSU), respectively. These three units are in turn sandwiched between two blueschist-facies units (the Pinerolo Unit, PU, at the bottom, and the Dronero-Sampeyre Unit, DSU, at the top). In contrast to the well-constrained P-T evolution of the BIU, peak P-T conditions for its bounding HP units are poorly constrained, most studies dating back to over 20 years ago and mostly relying on conventional thermobarometric methods. This study aims to update our knowledge about the P-T evolution experienced by the whole tectonometamorphic package of the southern DMM. For the first time, peak P-T conditions and prograde evolution for the five units (PU, SCU, BIU, RSU, DSU) forming the southern DMM tectonic "sandwich" are estimated using the same, internally consistent and therefore comparable, modern thermobarometric approaches. The study focuses on metapelites (i.e., garnet-bearing phengitic micaschists) and combines multi-equilibrium thermobarometry (Average PT) with the P-T pseudosection approach. Our results demonstrate that most of the southern DMM nappe stack (i.e., SCU, RSU and also the PU, that was originally considered as a blueschist-facies unit) experienced eclogite-facies metamorphism under similar peak P-T conditions (500-520°C, 20-24 kbar), and followed the same prograde path, suggesting similar burial mechanisms. The UHP BIU followed an early prograde evolution similar to that of the other eclogitic units of the southern DMM tectonic "sandwich". The attainment of UHP peak conditions occurred through an earlier steep, almost isothermal increase in pressure and a later increase in temperature. The DSU is the only unit of the southern DMM nappe stack that did not experience eclogite-facies metamorphism (peak metamorphism at blueschist-facies conditions: 450-470 °C, 17-18 kbar) and it is separated from the eclogitic units by a shear zone (the Valmala Shear Zone), whose interpretation requires further studies. These new data represent the inescapable starting point for any conceptual model aiming for a deeper understanding of the subduction/exhumation processes of UHP</p>

	continental units.
<b>Keywords:</b>	(U)HP metamorphism; southern Dora-Maira Massif; peak P-T conditions; prograde evolution; P-T pseudosections
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## Cover Page

Title: **What's in the sandwich? New P-T constraints for the (U)HP nappe stack of southern Dora-Maira Massif (Western Alps)**

Running title

**Prograde P-T evolution of (U)HP units in the southern DMM**

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## Abstract

The Brossasco-Isasca Unit (BIU) of the southern Dora-Maira Massif (DMM), Western Alps, is one of the most studied ultra-high pressure (UHP) units in the world. However, the interpretation of UHP metamorphism in the BIU is still a highly debated and challenging issue. The structural and tectonometamorphic setting of the southern DMM is described in the literature as a tectonic “sandwich”, with the UHP unit in the middle, bounded by two high-pressure (HP) eclogitic units in the footwall (the San Chiaffredo Unit, SCU) and hanging wall (the Rocca Solei Unit, RSU), respectively. These three units are in turn sandwiched between two blueschist-facies units (the Pinerolo Unit, PU, at the bottom, and the Dronero-Sampeyre Unit, DSU, at the top). In contrast to the well-constrained P-T evolution of the BIU, peak P-T conditions for its bounding HP units are poorly constrained, most studies dating back to over 20 years ago and mostly relying on conventional thermobarometric methods. This study aims to update our knowledge about the P-T evolution experienced by the whole tectonometamorphic package of the southern DMM. For the first time, peak P-T conditions and prograde evolution for the five units (PU, SCU, BIU, RSU, DSU) forming the southern DMM tectonic “sandwich” are estimated using the same, internally consistent and therefore comparable, modern thermobarometric approaches. The study focuses on metapelites (*i.e.*, garnet-bearing phengitic micaschists) and combines multi-equilibrium thermobarometry (Average PT) with the P-T pseudosection approach. Our results demonstrate that most of the southern DMM nappe stack (*i.e.*, SCU, RSU and also the PU, that was originally considered as a blueschist-facies unit) experienced eclogite-facies metamorphism under similar peak P-T conditions (500-520°C, 20-24 kbar), and followed the same prograde path, suggesting similar burial mechanisms. The UHP BIU followed an early prograde evolution similar to that of the other eclogitic units of the southern DMM tectonic “sandwich”. The attainment of UHP peak conditions occurred through an earlier steep, almost isothermal increase in pressure and a later increase in temperature. The DSU is the only unit of the southern DMM nappe stack that did not experience eclogite-facies metamorphism (peak metamorphism at blueschist-facies conditions: 450-470 °C, 17-18 kbar) and it is separated from the eclogitic units by a shear zone (the Valmala Shear Zone), whose interpretation requires further studies. These new data represent the inescapable starting point for any conceptual model aiming for a deeper understanding of the subduction/exhumation processes of UHP continental units.

## Key-words

(U)HP metamorphism; southern Dora-Maira Massif; peak P-T conditions; prograde evolution; P-T pseudosections

## 1. Introduction

The first discovery, more than 30 years ago, of coesite in continental crustal rocks (Chopin, 1984; Smith, 1984), demonstrated the possibility for continental crust to reach ultra-high pressure (UHP) conditions. However, the geodynamic processes responsible for the formation and exhumation of continental UHP units are still debated (*e.g.*, Schenker *et al.*, 2015; Reuber *et al.*, 2016; Solarino *et al.*, 2018). Conceptual and numerical models that try to explain how a continental crustal unit can reach (and can be exhumed from) UHP conditions are calibrated against geological and petrological data available from the tectonic nappe stack which includes the UHP unit itself (*e.g.*, Li *et al.*, 2010; Burov *et al.*, 2014; Schmalholz *et al.*, 2014; Gerya, 2015; Schenker *et al.*, 2015). Precise knowledge of peak pressure and temperature (P-T) conditions experienced by both the UHP unit and its adjacent, often high-P (HP) units is therefore the crucial starting point to test the validity of the models (*e.g.*, Manzotti *et al.*, 2015, 2018).

The Brossasco-Isasca Unit (BIU) of the southern Dora-Maira Massif (DMM) in Western Alps, is one of the most studied UHP units worldwide and has been widely used in the past as a natural laboratory to discover new UHP minerals and to investigate metamorphic processes occurring during subduction at extreme pressures (*e.g.*, Chopin & Ferraris, 2003; Schertl & O'Brien, 2013 and references therein). The models assuming subduction of continental crust to mantle depths (*e.g.*, Chemenda *et al.*, 1995; Chopin, 2003; Stöckhert & Gerya, 2005; Gerya & Stöckhert, 2006; Yamato *et al.*, 2008; Butler *et al.*, 2013) were proposed after the discovery of coesite in the BIU. Decades later, the alternative idea of tectonic overpressure explaining UHP tectonics arose again in the southern DMM (*e.g.*, Ford *et al.*, 2006; Schmalholz *et al.*, 2014; Schmalholz & Duretz, 2015; Schenker *et al.*, 2015). More than 30 years after its discovery, the interpretation of UHP metamorphism in the BIU still remains a challenge for many generations of geoscientists.

In the southern DMM, the UHP BIU is tectonically sandwiched between two quartz-eclogite facies units, the lower San Chiaffredo Unit (SCU) and the upper Rocca Solei Unit (RSU), which are in turn bounded by two blueschist-facies units, the Pinerolo Unit (PU) at the bottom and the Dronero-Sampeyre Unit (DSU) at the top of the tectonometamorphic package (Fig. 1). In contrast to the well-constrained P-T evolution of the BIU (*e.g.*, Ferrando *et al.*, 2017 and references therein), peak P-T conditions for its adjacent Units are poorly constrained, most studies dating back to over 20 years ago and mostly relying on conventional thermobarometric methods (*e.g.*, Chopin *et al.*, 1991; Michard *et al.*, 1993; Compagnoni *et al.*, 1995). Notably, many of these studies, which still represent milestones for all those interested in the interpretation of the tectonometamorphic evolution and architecture of the southern DMM, were carried out by Christian Chopin and co-workers. It is therefore a great pleasure for us to contribute to this Special Issue dedicated to Christian Chopin, with the aim of updating his legacy, taking advantage of the modern petrological methods and exploiting the great amount of data collected by our group over last decades.

With these premises in mind, this study constrains the prograde-to-peak evolution experienced by the HP units bounding the UHP BIU. For the first time, peak P-T conditions for all five units (PU, SCU, BIU, RSU, DSU) forming the southern DMM tectonic “sandwich” (Compagnoni & Rolfo, 2003) are estimated using the same, internally consistent and therefore comparable, modern thermobarometric approaches. The study focuses on metapelites (*i.e.*, garnet-bearing phengitic micaschists) because they are widely exposed in all the investigated units and preserve the (U)HP assemblages well. Thermobarometric estimates are obtained combining multi-equilibrium thermobarometry (Average PT) and/or the P-T pseudosection approach applied to five samples (one for each unit). Concerning the HP units bounding the UHP BIU, our results confirm peak-T already known from the literature, but indicate systematically higher peak-P. The prograde path of the BIU is also significantly revised, with possible implications for the interpretation of burial mechanisms in the whole southern DMM tectonic “sandwich”.

In our opinion, these new data represent the inescapable starting point for any model aimed at a deeper understanding of the processes responsible for the attainment and preservation of UHP conditions

in continental crust; however, further studies are needed in order to understand if (and how) the studied units shared part of their prograde evolution at HP to UHP conditions or if (and how) they were coupled during exhumation.

## 2. Geological setting

The Dora-Maira Massif (DMM) in the Western Alps, represents part of the subducted-exhumed European continental margin (*e.g.*, Michard *et al.*, 1996). It is now stacked in the Alpine orogenic wedge (Lardeaux *et al.*, 2006), wherein it was overthrust by meta-ophiolite units of the Piedmont Zone (Balestro *et al.*, 2018, and references therein). The southern portion of the DMM is a pile of imbricated thrust sheets, resulting from Alpine tectonic juxtaposition and metamorphic reworking of slices of Variscan continental crust and of Permian igneous bodies (*e.g.*, Vialon, 1966; Henry, 1990; Chopin *et al.*, 1991; Michard *et al.*, 1993, 1995; Turello, 1993; Sandrone *et al.*, 1993; Balestro *et al.*, 1995; Compagnoni *et al.*, 1995, 2012; Compagnoni & Rolfo, 1999, 2003; Groppo, 2002; Compagnoni *et al.*, 2004, 2012; Botta, 2015; Nosenzo, 2018). Relics of both amphibolite-facies Variscan metamorphism and Permian contact metamorphism are locally still preserved (*e.g.*, Biino & Compagnoni, 1992; Compagnoni *et al.*, 1995; Compagnoni & Rolfo, 2003; Groppo *et al.*, 2006, 2007b).

In the area between the Po Valley to the north and the Maira Valley to the south, the following tectonometamorphic units are distinguished from the lower to the upper structural position (Fig. 1): (i) the Pinerolo Unit (PU) is a monometamorphic unit that experienced Alpine epidote-blueschist facies metamorphism (*e.g.*, Chopin *et al.*, 1991; Avigad *et al.*, 2003); (ii) the San Chiaffredo Unit (SCU) is a portion of pre-Alpine continental crust (Variscan amphibolite-facies basement intruded by Permian granitoids) that reached quartz-eclogite facies peak during Alpine metamorphism (Compagnoni & Rolfo, 2003); (iii) the Brossasco-Isasca Unit (BIU) is lithologically similar to the SCU but experienced Alpine peak P-T conditions in the coesite-eclogite facies (diamond stability field; *e.g.*, Schertl *et al.*, 1991; Nowlan *et al.*, 2000; Rubatto & Hermann, 2001; Hermann, 2003; Ferraris *et al.*, 2005; Di Vincenzo *et al.*, 2006; Castelli *et al.*, 2007; Groppo *et al.*, 2007a; Ferrando *et al.*, 2009; Gauthiez-Putallaz *et al.*, 2016); (iv) the Rocca Solei Unit, lithologically similar to the BIU and the SCU, experienced Alpine peak P-T conditions at quartz-eclogite facies conditions (Chopin *et al.*, 1991; Matsumoto & Hirajima, 2000); (v) the Dronero-Sampeyre Unit (DSU) includes polymetamorphic schists (Henry, 1990; Chopin *et al.*, 1991) and a monometamorphic Permian volcano-detrital sequence (Vialon, 1966; Chopin *et al.*, 1991; Michard *et al.*, 1995), both of which experienced Alpine peak P-T conditions at epidote-blueschist facies (Chopin *et al.*, 1991). The DSU is separated from the structurally underlying RSU by a shear zone, hundreds of metres thick, consisting of the tectonic juxtaposition of meta-ophiolite and metasediment slices (Valmala Shear Zone; *i.e.*, the “ophiolitiferous band” of Henry *et al.*, 1993). The term “tectonic sandwich” is hereafter used to indicate the whole package of juxtaposed tectonometamorphic units of southern DMM described above. All these units have been overprinted by a late-Alpine greenschist-facies recrystallization, which pervasively reworked and extensively obliterated the former (U)HP metamorphic mineral assemblages.

Sample locations are reported in Fig. 1 and additional details are given in the Supplementary material.

## 3. Methods

### 3.1 Micro-X-ray fluorescence ( $\mu$ -XRF) maps

Qualitative major element X-ray maps of the entire thin sections were acquired using a micro-XRF Eagle III-XPL spectrometer equipped with an EDS Si(Li) detector and with an EdaxVision32 microanalytical system at the Department of Earth Sciences, University of Torino. Operating conditions were: 100 ms counting time, 40 kV accelerating voltage, and a probe current of 900  $\mu$ A. A spatial resolution of about 65  $\mu$ m in both x and



y directions was used. Quantitative modal amounts of each mineral phase were obtained by processing the maps with the software Petromod (Cossio *et al.*, 2002). For each sample, the processed X-ray maps are reported in Fig. 2. Additional microstructural details, at greater magnification, are given in Figs. 3-5. Mineral abbreviations are after Whitney & Evans (2010), except white mica (Wm) and phengite (Phe).

### 3.2 Mineral chemistry

The rock-forming minerals were analyzed with a Jeol JSMIT300LV Scanning Electron Microscope at the Department of Earth Sciences, University of Torino. The instrument was equipped with an energy dispersive spectrometry (EDS) Energy 200 system and an SDD X-Act3 detector (Oxford Inca Energy). Operating conditions were: 50 s counting time, 15 kV accelerating voltage, spot size 2  $\mu\text{m}$ . SEM-EDS quantitative data were acquired and processed using the Microanalysis Suite Issue 12, INCA Suite version 4.01; natural mineral standards were used to calibrate the raw data; the  $\phi\rho\rho Z$  correction (Pouchou & Pichoir, 1988) was applied. Tables SM1 and SM2-SM6, freely available online as Supplementary Material linked to this article on the GSW website of the journal, <https://pubs.geoscienceworld.org/eurjmin/>, summarize the compositional variations (Table SM1) and the representative chemical compositions for the main minerals in each sample; Figs. 6-7 and SM1 show the composition of garnet and phengite. For practical purposes, the term phengite is used in the following to indicate phengitic white mica with Si > 3.20 a.p.f.u. (on the basis of 11 oxygens), whereas muscovite is used for phengitic white mica with Si < 3.20 a.p.f.u.

### 3.3 Pseudosection modelling

The pseudosection modeling approach was applied to each metapelite sample, excluding DM1565. Bulk-rock composition of each sample (Table 1) was calculated by combining estimated mineral modes with mineral chemistry (see above). Determination of an effective bulk composition for sample DM1565 (DSU) was problematic because: (i) the fine-grained nature of Alpine Grt<sub>2</sub> hampered its correct quantification from micro-XRF maps; (ii) the presence of pre-Alpine garnet porphyroblasts (Grt<sub>1</sub>), that should be subtracted from the bulk-composition effectively reacting during Alpine metamorphism, makes the conventional bulk-rock analysis (e.g., XRF or ICP-MS) not suitable.

For each considered sample, three P-T isochemical phase diagrams have been calculated (*i.e.*, a total of 12 pseudosections) considering the fractionation effects on the bulk-composition due to the growth of zoned garnet porphyroblasts. Each pseudosection was used to model: (i) P-T conditions for garnet core growth (measured bulk-composition: MBC), (ii) P-T conditions for garnet mantle growth (MBC minus garnet cores), and (iii) P-T conditions for garnet rim growth (MBC minus garnet cores + mantles) (Table 1).

The P-T isochemical phase diagrams were calculated in the system MnNKCFMASTOH (MnO-Na<sub>2</sub>O-K<sub>2</sub>O-CaO-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O), except for sample DM1281 (BIU), for which Fe<sup>3+</sup> was neglected, because Fe<sup>3+</sup>-rich oxides are absent and the amount of Fe<sup>3+</sup> in the analyzed minerals is very low. The pseudosections were calculated using Perplex 6.8.1 (version March 2018; Connolly, 1990, 2005, 2009), the internally consistent thermodynamic dataset of Holland & Powell (2011) (ds62) and the equation of state for H<sub>2</sub>O of Holland & Powell (1998). The following solution models were used: garnet, chlorite, chloritoid, staurolite, white mica, biotite and ilmenite (White *et al.*, 2014), omphacite (Green *et al.*, 2007), amphibole (Green *et al.*, 2016), carpholite (Smye *et al.*, 2010), feldspar (Fuhrman & Lindsley, 1988) and epidote (Holland & Powell, 2011). Quartz, lawsonite, kyanite, rutile and titanite were considered as pure phases. The fluid was usually considered as pure H<sub>2</sub>O ( $a_{\text{H}_2\text{O}}=1$ ), but a reduced  $a_{\text{H}_2\text{O}}=0.4$  was considered in the pseudosection that models the garnet rim growth in DM1281 (BIU) because experimental and fluid inclusions studies (Sharp *et al.*, 1993; Hermann, 2003; Ferrando *et al.*, 2009) demonstrated that, at the UHP peak, the activity of H<sub>2</sub>O was strongly reduced by the abundance of dissolved species.

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### 3.4 Optimal thermobarometry

The THERMOCALC “Average PT” (AvPT) method (*i.e.*, “Optimal thermobarometry”: Powell & Holland, 1994) was applied to all the samples. THERMOCALC v3.40 and the Holland & Powell (2011) dataset (ds62) were used. Activity-composition relationships were calculated using the software AX. The method was applied to the peak assemblage for all the samples, except sample DM1281 (BIU), for which it was applied to the late prograde assemblage (see Section 4.3). Used sets of mineral compositions and of independent reactions are given in Tables SM2-SM7. AvPT results are discussed in terms of weighted means (*i.e.*, values with smaller errors contribute more than values with larger errors) and are presented in Table 2.

## 4. Petrography and mineral chemistry

### 4.1 Sample DM 1485 (PU)

This medium- to coarse-grained micaschist consists of white mica (mostly phengite; 42%), garnet (20%), chlorite (19%), quartz (13%) and minor chloritoid (2%) (Fig. 2). Retrograde chlorite, plagioclase (3%) and minor biotite, as well as accessory magnetite, rutile and ilmenite also occur. The main foliation ( $S_m$ ) is defined by preferred orientation of phengite and chlorite, that form continuous pluri-mm -thick layers alternated with discontinuous pluri-mm -thick quartzitic layers (Fig. 2). An earlier schistosity ( $S_{m-1}$ ), defined by the preferred orientation of white mica and chlorite, is still preserved in microlithons.

Garnet porphyroblasts, up to several millimetres in size, are syn-kinematic with respect to  $S_m$  and show a snow-ball structure (Fig. 3a); the rotated internal foliation, continuous with the external  $S_m$ , is defined by inclusions of quartz, relict chloritoid, and minor white mica and chlorite (Fig. 3b). Quartz, phengite and chlorite occur in the pressure shadows of garnet. Garnet porphyroblasts are strongly zoned (Fig. 6a and Table SM1), with a reddish core and a pinkish rim.

Phengite defines the  $S_m$  and rarely occurs, in association with paragonite and relict chloritoid, in polymineralic inclusions within garnet core and mantle (Fig. 3b). A few retrograde muscovite flakes occur in matrix and in polymineralic inclusions within garnet. Paragonite is only observed in polymineralic inclusions in garnet, always associated with (or replacing) chloritoid; its prograde vs. retrograde nature is ambiguous. Bluish-greenish chloritoid is only preserved as inclusions in garnet porphyroblasts (Fig. 3a,b), but not in the matrix. Its composition changes according to the microstructural position within garnet (Table SM1). Chlorite is mostly in equilibrium with  $S_m$ , but a late chlorite generation replaces garnet along fractures. Chlorite rim is locally partially replaced by fine-grained biotite. Plagioclase (albite to oligoclase) occurs as large (pluri-mm) blasts overgrowing the  $S_m$  and it is thus interpreted as a retrograde phase.

Among the accessories, retrograde mm-sized magnetite exclusively occurs in the matrix (Fig. 2). Rutile and ilmenite within garnet core, mantle and rim appear in equilibrium, whereas in the matrix rutile is rimmed by ilmenite.

### 4.2 Sample DM1667c (SCU)

This garnet-bearing phengitic micaschist has a strongly heterogeneous grain size. It shows a mm-thick banded structure, with continuous medium- to coarse-grained phengite-rich layers alternating with fine- to medium-grained discontinuous quartz-rich layers (Fig. 2). It consists of white mica (mostly phengite: 42%), garnet (30%), quartz (18%) and minor chloritoid (1%). Retrograde chlorite (7%), epidote (1%), minor biotite, and accessory magnetite, rutile, ilmenite, tourmaline and apatite also occur. The main foliation ( $S_m$ ) is defined by the preferred orientation of white mica.

Garnet porphyroblasts are centimetres to pluri-cm in size in the coarse-grained layers, and millimetres to pluri-mm in the finer-grained layers (Fig. 2). Garnet is pre- to syn-kinematic with respect to the

275  $S_m$ , being mostly enveloped by the main schistosity, but with the rim that appears in equilibrium with it.  
276 Garnet porphyroblasts are microstructurally and chemically zoned (Fig. 6b). Garnet core and mantle are large,  
277 often asymmetric, and crowded with inclusions, whereas rim is thin and with few inclusions. Fine-grained  
278 inclusions in garnet core consist of epidote (Fig. 3d), chlorite and chloritoid; inclusions in garnet mantle are  
279 medium-grained and mostly consist of chloritoid (Fig. 3c) and white mica. Garnet rim includes few phengite  
280 flakes and box-shaped pseudomorphs after former lawsonite, consisting of a fine-grained aggregate of  
281 epidote, muscovite, paragonite and chlorite (Fig. 3e). A thin (100-300  $\mu\text{m}$ ) and discontinuous outer rim  
282 slightly enriched in Mn has been interpreted as due to local retrograde re-equilibration.

283 Phengite defines the  $S_m$  and is locally included in garnet. Less abundant retrograde muscovite  
284 overgrows the main foliation and replaces chloritoid inclusions within garnet. Paragonite only occurs as  
285 inclusion in garnet, associated with (or replacing) chloritoid, and as pseudomorphs after probable lawsonite;  
286 therefore, it has been interpreted as both prograde and retrograde phase. Chloritoid is mostly included in  
287 garnet mantle (Fig. 3c), rarely in core and rim, and it is absent from the matrix. It is locally partially to  
288 completely replaced by an aggregate of white mica (muscovite  $\pm$  phengite + paragonite) (Fig. 3c).

289 Epidote and chlorite occur in two different generations. Prograde epidote (often with an allanitic  
290 core) and chlorite are included in garnet core and mantle (Fig. 3d). Retrograde epidote occurs as few fine-  
291 grained idiomorphs in matrix and in pseudomorphs after lawsonite included in garnet rim, whereas late chlorite  
292 mostly replaces garnet porphyroblasts along fractures and rims. Late biotite partially replaces white mica and  
293 chlorite at their rims.

294 Among accessories, mm-sized retrograde magnetite only occurs in the matrix. Rutile and ilmenite  
295 occur as inclusions within garnet porphyroblasts; in the matrix rutile is rimmed by ilmenite. Apatite and  
296 tourmaline are included in garnet.

297

#### 298 **4.3 Sample DM1281 (BIU)**

299 This sample consists of white mica (mostly phengite, 41%), quartz (24%), garnet (21%), kyanite (10%), jadeite  
300 (3%) and minor chloritoid, staurolite and chlorite (Fig. 2). Albite and pyrophyllite are retrograde phases,  
301 whereas rutile, tourmaline and apatite are the main accessory minerals. The grain size is markedly  
302 heterogeneous, with pluri-mm garnet and kyanite porphyroblasts set in a fine-grained matrix mostly  
303 consisting of phengite and quartz (Fig. 2). The main schistosity ( $S_m$ ) is defined by mm-thick, continuous  
304 phengitic layers, alternating with discontinuous quartzitic layers of similar thickness.

305 Garnet porphyroblasts are microstructurally and chemically zoned (Fig. 6c). Garnet core and mantle  
306 are large, often asymmetric, and crowded with inclusions, whereas rim is thin and with few inclusions (Fig.  
307 4a). Garnet rim appears in equilibrium with  $S_m$ . Inclusions in garnet core are fine-grained and polymineralic;  
308 garnet mantle includes both fine-grained polymineralic inclusions and medium-grained monocrystalline  
309 inclusions; garnet rim contains few medium-grained monocrystalline inclusions. Polymineralic inclusions in  
310 garnet core mostly consist of chloritoid, paragonite, chlorite, staurolite and rare muscovite, whereas those  
311 observed in garnet mantle contain also kyanite and does not contain potassic white mica (Fig. 4d,e).  
312 Monocrystalline inclusions in garnet mantle are represented by pseudomorphs after jadeite and glaucophane  
313 (Fig. 4f, g), kyanite and quartz, whereas those in garnet rim consist of kyanite, phengite and quartz.  
314 Polycrystalline aggregates of quartz surrounded by radial cracks, interpreted as deriving from inversion of  
315 coesite, are located at the transition between garnet mantle and rim (Fig. 4a).

316 Phengite defines the  $S_m$  and is locally included in garnet rim. Retrograde muscovite is scarce and its  
317 occurrence is limited to the pseudomorphs after jadeite and glaucophane. A few prograde muscovite flakes  
318 are preserved in the polymineralic inclusions within garnet core. Paragonite is common in the polymineralic  
319 inclusions hosted within garnet core and mantle (Fig. 4e), where it probably has a prograde nature.

320 At least three different generations of kyanite have been recognized: i) large (pluri-mm)  
321 porphyroblasts enveloped by the main foliation (Fig. 4b); ii) smaller idioblasts in equilibrium with the  $S_m$  (Fig.  
322 4b); iii) local very fine-grained acicular crystals rimming the large kyanite porphyroblasts. Jadeite and  
323 glaucophane are not preserved, but are pseudomorphically replaced by retrograde phases. Pseudomorphs  
324 after jadeite, occurring both in the matrix (Fig. 4c) and as inclusion in garnet mantle (Fig. 4g), consist of a very  
325 fine-grained aggregate of albite + pyrophyllite + muscovite. Lozenge-shaped pseudomorphs after  
326 glaucophane have been observed only as inclusions in garnet mantle (Fig. 4f) and consist of a very fine-  
327 grained aggregate of paragonite + muscovite + minor biotite.

328 Chloritoid, chlorite and staurolite only occur in the fine-grained polymineralic inclusions within garnet  
329 core and mantle (Fig. 4d,e). Chlorite is a prograde phase and the  $X_{Mg}$  of the chlorite included in garnet mantle  
330 is higher than that of the chlorite included in garnet core (Table SM1). Chloritoid is generally associated with  
331 paragonite and chlorite. Staurolite is only present as inclusion in both garnet core and mantle, where it mostly  
332 occurs in association with kyanite, paragonite and chlorite, more rarely with chloritoid. Microstructural  
333 relationships clearly show that staurolite grew at the expense of kyanite, often preserved as rounded relics  
334 partially rimmed by staurolite (Fig. 4e).

335 Accessory rutile, tourmaline and apatite occur in the matrix and as inclusion in garnet  
336

#### 337 4.4 Sample DM1504 (RSU)

338 This fine- to coarse-grained, garnet-bearing phengitic micaschist consists of white mica (mostly phengite, 49  
339 % and paragonite, 6%), quartz (20%), chloritoid (12%) and garnet (8%) (Fig. 2), with minor amounts of  
340 glaucophane and jadeite (almost completely replaced by retrograde phases). Retrograde chlorite (3%),  
341 epidote (1%) and biotite, and accessory rutile, ilmenite, magnetite and apatite also occur. The main foliation  
342 ( $S_m$ ) is defined by mm- to pluri-mm -thick, continuous, micaceous layers alternated with mm-thick,  
343 discontinuous, quartzitic layers. Relics of an earlier  $S_{m-1}$  schistosity are locally preserved in microlithons and  
344 are defined by the alignment of white mica.

345 Mm- to pluri-mm -sized garnet porphyroblasts are partially enveloped by the  $S_m$ , but their rim  
346 appears in equilibrium with  $S_m$  (i.e., garnet is pre- to syn-kinematic with respect to  $S_m$ ). They include an  
347 internal rotated foliation mostly defined by quartz and chloritoid. Garnet core and mantle are large and rich  
348 of inclusions, whereas garnet rim is thin and with few inclusions (Fig. 5a-c). Inclusions in garnet are either  
349 polymineralic or monocrystalline. Polymineralic inclusions mostly consist of chloritoid + white micas  
350 (phengite  $\pm$  paragonite  $\pm$  muscovite) (Fig. 5b). Relics of glaucophane + jadeite, partially replaced by paragonite  
351 + albite  $\pm$  muscovite, have been observed at the transition between garnet mantle and garnet rim (Fig. 5b).  
352 Garnet core and mantle locally include tabular-shaped aggregates of epidote + quartz + paragonite or  
353 phengite (Fig. 5c), possibly representing pseudomorphs after former lawsonite. Monocrystalline inclusions  
354 mostly consist of quartz, chloritoid and minor phengite.

355 Phengite defines the  $S_m$  and is locally included in garnet and chloritoid. Retrograde paragonite and  
356 muscovite occur both in the matrix and as inclusions in garnet. In the matrix, paragonite forms large flakes  
357 statically overgrowing the  $S_m$  (Fig. 2). When included in garnet, paragonite and muscovite generally replace  
358 other phases, such as glaucophane, jadeite or chloritoid. Chloritoid occurs both in the matrix and as inclusion  
359 in garnet (Fig. 5a). In the matrix, it forms medium-grained bluish-greenish nematoblasts aligned with the  $S_m$   
360 and it is slightly zoned. Rare glaucophane and jadeite relics are included in garnet mantle/rim (Fig. 5b).

361 Epidote, chlorite, albite and biotite are retrograde phases. Epidote within garnet occurs in tabular-  
362 shaped aggregates, in association with quartz and white micas, interpreted as deriving from former lawsonite  
363 (Fig. 5c). In the matrix, it forms few fine-grained idioblasts, often with an allanitic core. Aggregates of chlorite  
364 statically overgrows the  $S_m$  and replaces garnet along fractures and at the rim. Its rim is locally replaced by  
365 biotite. Albite occurs as replacement of jadeite and glaucophane.

Rutile mostly occurs as inclusion in garnet, whereas it is pervasively replaced by ilmenite in the matrix. Retrograde magnetite is fine-grained and widespread in the matrix, and it is strongly oxidized. Apatite occurs as relatively large grains both in the matrix and included in garnet.

#### 4.5 Sample DM1565 (DSU)

This garnet-bearing phengitic micaschist consists of white mica (mostly phengite, 54% and paragonite, 8%), quartz (26%), garnet (5%) and chloritoid (3%) (Fig. 2). Retrograde chlorite (3%) and biotite and accessory rutile, ilmenite and tourmaline also occur. The main schistosity ( $S_m$ ) is defined by pluri-mm thick, continuous, micaceous layers alternating with mm-thick quartzitic layers. Large (pluri-mm) garnet porphyroblasts are preferentially set in the fine-grained micaceous layers (Fig. 2).

In contrast to the other samples, this metapelite preserves mineralogical evidence of a polymetamorphic evolution. Two different garnet generations can be, in fact, recognized: (i) large porphyroblasts (Fig. 5d) enveloped by the  $S_m$ , interpreted as amphibolite-facies Variscan garnets ( $Grt_1$ ); (ii) small (ca. 100  $\mu m$ ) idioblasts in equilibrium with  $S_m$  and a thin and discontinuous corona around porphyroblastic  $Grt_1$  (Fig. 5e), both interpreted as Alpine garnets ( $Grt_2$ ). The strongly-fractured  $Grt_1$  is chemically zoned (Table SM1). Locally it is poikiloblastic and includes quartz, white mica, ilmenite and minor staurolite, now replaced by fine-grained pseudomorphic aggregates of white mica + chloritoid. The small  $Grt_2$  idioblasts are also zoned and include very fine-grained quartz (Fig. 6e and Table SM1).

Phengite defines the  $S_m$  and it also occurs at the rim of the chloritoid-bearing pseudomorphs after former staurolite. Minor retrograde muscovite and paragonite occur in the matrix. Chloritoid mostly constitutes large (pluri-mm) fine-grained aggregates enveloped by the  $S_m$  and interpreted as pseudomorphs after pre-Alpine porphyroblastic staurolite (Fig. 5f) (see also Henry, 1990; Chopin *et al.*, 1991). These pseudomorphs also contain white mica (phengite + muscovite + paragonite), generally concentrated toward the rim. Chloritoid also forms minor idioblasts aligned with the  $S_m$  or partially overgrowing it.

Retrograde chlorite occurs as large flakes statically overgrowing the  $S_m$  and partially replacing garnet at the rim and along fractures. Biotite is limited to late and discontinuous shear bands crosscutting the main foliation. Accessory ilmenite is included in pre-Alpine garnet ( $Grt_1$ ) and is rimmed by rutile, if it communicates with the external matrix through fractures. In the matrix, rutile is rimmed by ilmenite.

#### 5. Resulting P-T evolution

The prograde-to-peak P-T evolution of the PU, SCU, BIU and RSU samples was constrained using the pseudosection approach and on the basis of the predicted stability fields of the observed mineral assemblages, combined with garnet, chloritoid and phengite compositional isopleths. The results of thermodynamic modelling show that the fractionation effects on the bulk-composition due to the growth of zoned garnet porphyroblasts are generally minor during the initial growth of garnet (*i.e.*, after the fractionation of garnet core). However, they become significant after the fractionation of both garnet core and mantle. The general topology of the calculated pseudosections for all samples is similar as far as the relationships between the main phases of interest is concerned, and is in line with previous studies related on phase equilibria modeling in the same system (*e.g.*, Guiraud *et al.*, 1990; Proyer, 2003; Wei & Powell, 2004, 2006; Smye *et al.*, 2010; Manzotti *et al.*, 2015): (i) garnet is always stable over a large range of P-T conditions, whereas chlorite is limited to  $P < 18-25$  kbar; (ii) chloritoid is stable at  $T < 550-600^\circ C$ , and kyanite is instead stable at increasing temperature (see Smye *et al.*, 2010); (iii) paragonite, glaucophane and jadeite represent the Na-rich phases stable at lower, intermediate and higher pressure, respectively.

The Average PT approach of THERMOCALC was further applied to peak assemblages for the PU, SCU, RSU and DSU samples and to the late prograde assemblage for the BIU sample. In the following, the results of both approaches are summarized.

### 5.1 Sample DM1485 (PU)

The observed prograde and peak assemblage (Qz + Phe + Grt + Chl + Cld + Rt + Ilm) is not modeled in the P-T region of interest because chloritoid is always predicted to be stable with a Na-rich phase (either paragonite or glaucophane), which was not observed in the studied sample. However, the occurrence of large oligoclase porphyroblasts in the matrix statically overgrowing the main foliation suggests that one or more Na-rich phases (e.g. glaucophane, paragonite) was likely stable in the prograde and peak assemblages and it is not preserved. The glaucophane/paragonite-bearing assemblage (Qz + Phe + Grt + Chl + Cld + Gln/Pg + Rt + Ilm) is modeled in a wide range of P-T conditions (450-570°C, 10-25 kbar) (Fig. 8).

Prograde and peak P-T conditions are more tightly constrained by the intersection of compositional isopleths. Specifically: (i) early prograde P-T conditions are constrained at 480-495°C, 19-21 kbar using compositions of garnet core ( $\text{Sps}_{5.5}\text{Prp}_{6.5}\text{Grs}_{8.5}\text{Alm}_{80}$ ) and of its inclusions of chloritoid ( $X_{\text{Mg}}=0.11$ ) and phengite ( $\text{Si}=3.48$  a.p.f.u.) (Fig. 8a); (ii) late prograde P-T conditions are constrained at 490-505°C, 20-22 kbar using the compositions of garnet mantle ( $\text{Sps}_{2.5}\text{Prp}_{6.5}\text{Grs}_{7.5}\text{Alm}_{81}$ ) and of its inclusions of chloritoid ( $X_{\text{Mg}}=0.15$ ) and phengite ( $\text{Si}=3.44$ - $3.45$  a.p.f.u.) (Fig. 8b); (iii) peak P-T conditions are estimated at 500-515°C, 20-23 kbar using the compositions of garnet rim ( $\text{Sps}_{0.5}\text{Prp}_{11}\text{Grs}_{11}\text{Alm}_{78}$ ), of its chloritoid inclusions ( $X_{\text{Mg}}=0.18$ ) and of matrix phengite ( $\text{Si}=3.38$ - $3.51$  a.p.f.u.) (Fig. 8c).

The AvPT approach applied to four different sets of mineral compositions gives peak P-T conditions of  $496 \pm 7$  °C,  $19.0 \pm 0.7$  kbar (Table 2), consistent with the results of pseudosection modeling (Fig. 8c).

### 5.2 Sample DM1667c (SCU)

Although glaucophane was not observed in prograde and peak assemblages, the modeled pseudosections predict its stability over a large P-T interval. However, the predicted modal amount of glaucophane is so low (< 5 vol%) that its (former) occurrence could likely have been overlooked. Ignoring glaucophane, the observed early prograde (Qz + Phe + Grt<sub>C</sub> + Chl + Cld + Ep + Rt + Ilm) and late prograde (Qz + Phe + Grt<sub>M</sub> + Cld ± Chl ± Ep/Lws + Rt + Ilm) assemblages are modeled by large tri- and quadri-variant fields at 420-500°C, 12-17 kbar and 400-500°C, 14-25 kbar, respectively (Fig. 9). Garnet, chloritoid and phengite compositional isopleths allow to further constrain the prograde P-T conditions: (i) early prograde conditions are constrained at 460-470°C, 17-19 kbar using the compositions of garnet core ( $\text{Sps}_{5.5}\text{Prp}_{3.5}\text{Grs}_{26}\text{Alm}_{65}$ ) and its inclusions of phengite ( $\text{Si}=3.34$ - $3.46$  a.p.f.u.) (Fig. 9a); (ii) late prograde P-T conditions are constrained at 480-490°C, 19-21 kbar using the compositions of garnet mantle ( $\text{Sps}_{2.5}\text{Prp}_{5}\text{Grs}_{24}\text{Alm}_{68}$ ) and of its inclusions of chloritoid ( $X_{\text{Mg}}=0.20$ ) and phengite ( $\text{Si}=3.40$ - $3.49$  a.p.f.u.) (Fig. 9b). Although garnet core includes epidote, its growth is predicted to occur within the lawsonite stability field, but close to the Ep-out boundary.

The observed peak assemblage (Qz + Phe + Grt<sub>R</sub> + Cld + Lws + Rt + Ilm) is modeled by a relatively small quadri-variant field at 450-520°, 22-27 kbar. The intersection of compositional isopleths for garnet rim ( $\text{Sps}_{0.8}\text{Prp}_{10}\text{Grs}_{18}\text{Alm}_{74}$ ) and its inclusions of chloritoid ( $X_{\text{Mg}}=0.20$ ) and phengite ( $\text{Si}=3.36$ - $3.43$  a.p.f.u.) defines peak P-T conditions at 500-520°C, 21-24 kbar (Fig. 9c). The AvPT approach applied to four different sets of mineral compositions gives peak P-T conditions of  $512 \pm 8$  °C,  $21.9 \pm 0.9$  kbar (Table 2), consistent with the results of pseudosection modeling (Fig. 9c).

### 5.3 Sample DM1281 (BIU)

Garnet core and its inclusions define the early prograde assemblage (Qz + Phe + Grt<sub>C</sub> + Cld + Pg + Chl + Rt). Staurolite is not considered as part of this assemblage due to its supposed retrograde nature (see microstructural relationships presented in Section 4.3). This assemblage is modeled by a quadri-variant field at 450-570°C, 10-18 kbar. The best fit between observed and modeled garnet (Sps<sub>6.5</sub>Prp<sub>12</sub>Grs<sub>6</sub>Alm<sub>74</sub>), chloritoid (X<sub>Mg</sub>=0.25) and chlorite (X<sub>Mg</sub>=0.62) compositions constrains P-T conditions for the growth of garnet core at 520-540°C, 16-23 kbar (Fig. 10a), in the Qz + Phe + Grt + Cld + Pg ± Chl ± Gln + Rt fields. These P-T conditions are at significantly lower T and higher P than the predicted stability field of staurolite, further confirming that staurolite is not compatible with the early prograde assemblage (see Section 4.3).

The late prograde assemblage consists of garnet mantle and its inclusions (Qz/Coe + Phe + Grt<sub>M</sub> + Cld + Pg + Ky + Jd + Gln + Rt); once again staurolite is not considered as part of this assemblage. Pseudomorphs after coesite are hosted in the outermost mantle domain, at the transition between Grt<sub>M</sub> and Grt<sub>R</sub>, suggesting that garnet mantle already grew at UHP conditions. The coexistence of chloritoid + kyanite constrains the temperature to a very narrow range (540-560°C), whereas the coexistence of jadeite, glaucophane and paragonite in the same garnet domain limits the pressures to the interval 24-28 kbar, *i.e.*, close to the transition between paragonite-bearing and jadeite-bearing fields (Fig. 10b). The modeled garnet (Sps<sub>1.5</sub>Prp<sub>19</sub>Grs<sub>2</sub>Alm<sub>76</sub>) and chloritoid (X<sub>Mg</sub>=0.30) compositional isopleths intersect within these fields and tightly constrain the late prograde P-T conditions at 540-560°C, 25-30 kbar, *i.e.*, at the transition between the quartz and coesite stability fields (Fig. 10b). This is consistent with the observed occurrence of polycrystalline aggregates of quartz after coesite at the transition between garnet mantle and rim. The AvPT approach applied to four different sets of mineral compositions gives late prograde P-T conditions of 557 ± 5 °C, 27.4 ± 0.4 kbar (Table 2), consistent with the pseudosection results (Fig. 10b).

The peak assemblage (Coe + Phe + Grt<sub>R</sub> + Ky + Jd + Rt) is modelled by a large penta-variant field at T > 530°C and P > 25 kbar. Although garnet (Sps<sub>1.7</sub>Prp<sub>26</sub>Grs<sub>3.5</sub>Alm<sub>68</sub>) compositional isopleths are far apart, their intersection with phengite (Si = 3.45-3.49 a.p.f.u.) isopleths allows constraining peak P-T conditions at 660-730°C and 38-43 kbar (Fig. 10c), consistent with the peak P-T conditions proposed in previous papers and based on other lithologies (*i.e.*, pyrope-bearing whiteschists, eclogites, marbles; see review in Ferrando *et al.*, 2017). The AvPT approach applied on the peak assemblage did not converge to a result, because its variance is too high to define enough reactions.

481

#### 482 **5.4 Sample DM1504 (RSU)**

The observed prograde and peak assemblage (Qz + Phe + Grt + Cld + Gln + Jd + Lws? + Rt) is modelled by a large quadri-variant field at 450-540°C, 19-25 kbar. The modelled garnet, chloritoid and phengite compositional isopleths intersect within this field and constrain prograde and peak P-T conditions as follows: (i) early prograde conditions are constrained at 490-510°C, 20-23 kbar using the compositions of garnet core (Sps<sub>9</sub>Prp<sub>8.5</sub>Grs<sub>16</sub>Alm<sub>67</sub>), of its chloritoid inclusions (X<sub>Mg</sub>=0.20) and of phengite (Si=3.31-3.43 a.p.f.u.) (Fig. 11a); (ii) late prograde conditions are constrained at 500-520°C, 20-24 kbar using the compositions of garnet mantle (Sps<sub>6</sub>Prp<sub>9.5</sub>Grs<sub>20</sub>Alm<sub>64</sub>), of its chloritoid inclusions (X<sub>Mg</sub>=0.22) and of phengite (Si=3.31-3.43 a.p.f.u.) (Fig. 11b); (iii) peak conditions are estimated at 510-525°C, 20-23 kbar using the compositions of garnet rim (Sps<sub>4.5</sub>Prp<sub>9</sub>Grs<sub>18.5</sub>Alm<sub>68</sub>), its chloritoid inclusions (X<sub>Mg</sub>=0.24) and phengite (Si=3.31-3.43 a.p.f.u.) (Fig. 11c). The AvPT approach applied to four different sets of mineral compositions gives peak conditions of 495 ± 8 °C, 20.3 ± 0.6 kbar (Table 2), consistent with pseudosection results (Fig. 11c).

494

#### 495 **5.5 Sample DM1565 (DSU)**

(Alpine) peak P-T conditions for this sample were estimated using the AvPT approach, applied to three different sets of mineral compositions. Although not observed in the sample, lawsonite was included in the peak assemblage, allowing to consider the reactions involving grossular, which are relevant because garnet

is relatively enriched in this component. This strategy is supported by the fact that other metapelites from the same unit show unambiguous evidence for the occurrence of lawsonite in the peak assemblage (Nosenzo, 2018). The AvPT results point to peak P-T conditions of  $452 \pm 8$  °C,  $17.2 \pm 0.4$  kbar (Table 2).

## 6. Discussion

### 6.1 New constraints on the prograde evolution of the tectonic units in the southern DMM

#### 6.1.1 Prograde evolution of the HP units bounding the UHP BIU

The prograde P-T evolution inferred for the four units bounding the UHP BIU is summarized below:

- The PU experienced a prograde evolution starting in the lawsonite-blueschist facies and reaching peak conditions in the eclogite-facies (500-515°C, 20-23 kbar; Fig. 12a). Peak-T conditions are similar to those estimated by Avigad *et al.* (2003) (*i.e.*, 530 °C) using multi-equilibrium thermobarometry applied on garnet-bearing metapelites from the same structural position. However, peak-P conditions are significantly higher than the 14-16 kbar estimated by the same authors (Fig. 12a).
- The P-T prograde path inferred for the SCU and RSU is remarkably similar to that constrained for the PU, with eclogite-facies peak P-T conditions at 500-520°C, 20-24 kbar (Fig. 12b, d). The estimated peak-P conditions are significantly higher than those (500-550°C, 15 kbar) constrained by Chopin *et al.* (1991) and Compagnoni & Rolfo (2003), whereas peak-T are in agreement with literature data (Fig. 12b, d).
- In contrast to the other units, the DSU did not experience eclogitic metamorphism. Estimated peak conditions (450-470 °C, 17-18 kbar) point to lawsonite-blueschist facies conditions (Fig. 12e); peak-T are similar to those reported by Chopin *et al.* (1991) (500°C, 10-12 kbar), but pressures are significantly higher (Fig. 12e).

Overall, our new data for the HP units bounding the UHP one substantially confirm peak-T already estimated more than 25 years ago, but point to a significant increase of peak-P estimates ( $\Delta P = 5-10$  kbar). This is the same trend already followed in the definition of peak P-T conditions for the UHP BIU, that were initially estimated to be at about 30 kbar (*e.g.*, Chopin *et al.*, 1991; Compagnoni *et al.*, 1995) and progressively increased (35 kbar: *e.g.*, Compagnoni & Rolfo, 2003) up to 40-43 kbar (*e.g.*, Hermann, 2003; Castelli *et al.*, 2007; Groppo *et al.*, 2007a; Ferrando *et al.*, 2009, 2017), in parallel with the progressive improvement of thermodynamic modeling approaches that extended the limits of conventional thermobarometry.

#### 6.1.2 A revised prograde P-T path for the UHP BIU

Peak P-T conditions (730°C, 40-43 kbar) and retrograde evolution of the UHP BIU are now very well defined and were constrained in the last decades through detailed petrological studies on a great variety of lithologies, among them pyrope-bearing whiteschists (Schertl *et al.*, 1991; Hermann, 2003; Ferrando *et al.*, 2009; Gauthiez-Putallaz *et al.*, 2016), eclogites (Nowlan *et al.*, 2000; Di Vincenzo *et al.*, 2006; Groppo *et al.*, 2007a), marbles and calc-silicate rocks (Rubatto & Hermann, 2001; Ferraris *et al.*, 2005; Di Vincenzo *et al.*, 2006; Castelli *et al.*, 2007). Garnet-bearing metapelites have never been used to constrain the BIU peak P-T conditions and have only been marginally used to constrain its retrograde evolution (Groppo *et al.*, 2006). This is due to the fact that the highly variant assemblage (*i.e.*, Coe + Phe + Grt + Ky + Jd) stable at UHP conditions is not suitable for application of conventional thermobarometry. Conversely, metapelites have been already used to constrain the early prograde evolution of the BIU, thanks to the preservation of abundant prograde inclusions in the core of porphyroblastic garnets. Chopin *et al.* (1991) and Michard *et al.* (1993) described a garnet-bearing phengitic micaschist (sample DM8412) very similar to our sample DM1281. Both their and our garnet porphyroblasts are, in turn, remarkably similar to the cores of the “superzoned” garnets described by Compagnoni & Hirajima (2001) (sample DM880). Chopin *et al.* (1991) and Compagnoni



& Hirajima (2001) interpreted the coexistence of chloritoid, kyanite, staurolite and chlorite in the polyminerale inclusions hosted within garnet cores as evidence that the BIU prograde trajectory passed close to the invariant point involving Cld + Ky + St + Chl, located around 600°C, 15 kbar. This was considered as a pinning point for the BIU prograde path for more than 25 years, resulting in a steep prograde trajectory located at temperatures significantly higher than the peak-T conditions estimated at that time for the adjacent units.

Our study unambiguously demonstrates that staurolite in the polyminerale inclusions hosted within garnet core and mantle has a retrograde nature, growing at the interface between garnet and kyanite, the latter mineral preserving a rounded/corroded shape (Fig. 4e). We suggest that staurolite grew during the retrograde evolution through a reaction that involved garnet, kyanite and chlorite as reactants. The aqueous fluid needed to trigger the reaction would not have been necessarily introduced from outside through fractures, but it could derive from the breakdown of chlorite associated with kyanite in the polyminerale inclusion (*i.e.*, internally-derived fluid). Reaction modelling by the least square method (freeware application available on demand; Godard, 2009) applied to the composition of garnet core/mantle, chlorite, kyanite and staurolite yielded balanced reactions of this type: Chl + Ky + Grt = St (details are given in Table SM8), accounting for the retrograde formation of staurolite in a closed system, *i.e.* the polyminerale inclusion. The above-mentioned reaction is predicted to occur in the KFMASH system at about 600-650 °C, 13-15 kbar (White *et al.*, 2014), and it would have been therefore intersected during the retrograde evolution of the BIU (Fig. 12c). It is worth noting that the growth of retrograde staurolite was already observed in the matrix of a garnet-bearing metapelite from the BIU, and was constrained exactly at these P-T conditions (Groppo *et al.*, 2006).

The new interpretation of the nature of staurolite occurring in the polyminerale inclusions hosted in the BIU garnet porphyroblasts has important consequences for the definition of the BIU prograde P-T path. The results of thermodynamic modeling and AvPT tightly constrain the growth of garnet core at 520-540°C, 16-23 kbar, *i.e.*, at significantly lower T and higher P than previously estimated, and at P-T conditions close to the peak P-T conditions of the adjacent units. Moreover, the growth of garnet mantle is modeled at UHP conditions, consistent with the occurrence of pseudomorphs after coesite included in the mantle domain. The whole prograde evolution of the BIU is thus significantly different from that previously assumed; it does not follow a regularly steep P/T gradient, but it is rather characterized by: (i) an early prograde evolution along a moderately steep P/T gradient, similar to that followed by the adjacent HP units; (ii) an intermediate steep, almost isothermal, pressure increase, and (iii) a late prograde temperature increase along a moderately steep P/T gradient, still at increasing pressure.

## 6.2 Implications for the geodynamic interpretation of the southern DMM

An in-depth discussion of the geodynamic processes responsible for the architecture of the southern DMM is beyond the aim of this paper. However, the following conclusions are worth noting and could represent new constraints for future investigations:

- (1) the PU experienced eclogite-facies metamorphism under peak P-T conditions very similar to those registered by the SCU and RSU (500-520°C, 20-24 kbar). Moreover, the PU, SCU and RSU units followed the same prograde path, along a medium T/P gradient of about 12°C kbar<sup>-1</sup>, suggesting similar burial mechanisms. The similarity of the peak P-T conditions experienced by the PU and SCU, combined with the fact that the PU sample was collected from an outcrop located very close to the contact with the BIU (Fig. 1), could potentially raise the doubt that the two samples actually belong to the same unit (*i.e.*, SCU). The contact between the PU and overlying units (either SCU or BIU) has been located thanks to the abrupt occurrence, moving downward in the DMM nappe stack, of abundant graphitic micaschists with quartzite intercalations (see Fig.1). These micaschists have never been described within the other units (either

SCU, BIU or RSU) and, in turn, have been considered diagnostic of the former PU (e.g., Vialon, 1966; Chopin *et al.*, 1991; Avigad *et al.*, 2003). Following this criterion, sample DM1485 has been attributed to the PU. Our results thus highlight that, in the investigated area, the PU does not correspond to a blueschist unit, as previously described (Avigad *et al.*, 2003), and therefore the actual occurrence of a blueschist unit stacked below an eclogitic ones has to be restricted to northernmost sectors of the DMM (*i.e.*, the Briançonnais-like tectonic window in the Pinerolo area; *e.g.*, Manzotti *et al.*, 2016).

(2) the UHP BIU seems to have followed an early prograde evolution similar to that of the other eclogitic units of the southern DMM tectonic “sandwich”. The attainment of UHP peak conditions occurred through an earlier almost isothermal increase in pressure ( $\Delta P=8-10$  kbar) along a significantly lower T/P gradient (ca.  $3^{\circ}\text{C kbar}^{-1}$ ) and a later increase in temperature ( $\Delta T=150-170^{\circ}\text{C}$ ) along a medium T/P gradient (ca.  $15^{\circ}\text{C kbar}^{-1}$ ). Our results suggest that UHP metamorphism was not the result of a single, homogeneous, process, but rather the product of a two-step process. Further geochronological studies are needed in order to test if the UHP BIU shared a synchronous prograde evolution with the adjacent eclogitic units.

(3) the DSU is the only unit of the southern DMM tectonic “sandwich” that, according to our results, did not experience eclogite-facies metamorphism. It is worth noting that, on the field, the DSU is separated from the eclogitic units by a hundreds of metres thick shear zone (tectonic *mélange sensu* Festa *et al.*, 2019), which includes slices of meta-ophiolite (Valmala Shear Zone: Nosenzo, 2018). The detailed description and interpretation of this shear zone is beyond the aim of this paper and further studies are necessary to understand its role in decoupling the southern DMM during subduction and/or in driving exhumation of related (U)HP units.

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811

## 812 Figure captions

813 **Fig. 1** – Simplified geological map (a) of the southern Dora-Maira Massif around the UHP Brossasco-Isasca  
 814 Unit (modified from Compagnoni *et al.*, 2012, and with unpublished data from Botta, 2015, and Nosenzo,  
 815 2018). Sample locations are shown by black stars both in the map and cross sections. The Polymetamorphic  
 816 and Monometamorphic Complexes in the SCU, BIU, RSU and DSU refer to a Variscan amphibolite-facies  
 817 metamorphic basement and to Permian igneous bodies, respectively, each of which reworked during Alpine  
 818 metamorphism. The insets (b, c) show the location of the southern DMM in north-west Italy (b) and within a  
 819 simplified tectonic sketch-map of the Western Alps (c).

821 **Fig. 2** – Processed micro-XRF maps of the studied metapelites. For sample DM1565 (DSU), Grt<sub>c</sub> and Grt<sub>M</sub> refer  
 822 to pre-Alpine Grt<sub>1</sub> porphyroblasts, whereas Alpine Grt<sub>2</sub> idioblasts in the matrix are reported as Grt<sub>R</sub>. Dark-  
 823 grey to black domains are holes in the thin sections (*i.e.*, pixels not assigned to mineral phases).

825 **Fig. 3** – Representative microstructures of samples DM1485 (a, b) and DM1667c (c-e) from the PU and SCU,  
 826 respectively. Sample DM1485: (a) Garnet porphyroblast with a snow-ball structure including quartz and  
 827 chloritoid. The plagioclase porphyroblasts in the matrix are related to retrogression. (b) Detail of chloritoid +  
 828 phengite + paragonite polymineralic inclusion in garnet mantle. Sample DM1667c: (c) Detail of chloritoid  
 829 included in garnet mantle, partially replaced by white mica. (d) Fine-grained epidote included in garnet  
 830 mantle. (e) Box-shaped pseudomorph after lawsonite included in garnet rim, consisting of epidote + phengite  
 831 + paragonite + chlorite. (a, b, c: Plane Polarized Light, PPL; d, e and insets in a, b; Crossed Polarized Light,  
 832 XPL).

834 **Fig. 4** – Representative microstructures of sample DM1281 from the BIU. (a) Zoned garnet porphyroblast,  
 835 with a large core and mantle crowded with fine-grained inclusions, and a thin rim with few inclusions. The  
 836 main foliation is defined by phengite. The inset shows a pseudomorph after coesite, consisting of  
 837 polycrystalline quartz, included in garnet mantle. (b) Detail of a pluri-mm kyanite porphyroblast (Ky<sub>1</sub>)  
 838 enveloped by the main foliation. Small idioblasts of Ky<sub>2</sub> are in equilibrium with the S<sub>m</sub>. (c) Pseudomorph after  
 839 jadeite, consisting of a fine-grained aggregate of albite, pyrophyllite and paragonite. (d) Fine-grained  
 840 polymineralic inclusions in garnet mantle. The inset shows a polymineralic inclusion in garnet core: note the  
 841 equilibrium relations among chloritoid, chlorite and paragonite. (e) Details of polymineralic inclusions in  
 842 garnet mantle, consisting of kyanite, staurolite, paragonite and chlorite. Staurolite systematically separates  
 843 corroded/rounded kyanite grains from garnet, suggesting that its growth is related to a reaction between  
 844 garnet and kyanite. (f, g) Pseudomorphs after glaucophane (f) and jadeite (g) included in garnet mantle,  
 845 consisting of fine-grained aggregates of paragonite + muscovite ± biotite and albite + pyrophyllite +  
 846 paragonite, respectively. (a, b, c, f, g: XPL; c, d: PPL; e and inset in d: Back Scattered Electron image, BSE).

848 **Fig. 5** – Representative microstructures of samples DM1504 (a-c) and DM1565 (d-f) from the RSU and DSU,  
 849 respectively. Sample DM1504: (a) Garnet porphyroblast with quartz and chloritoid inclusions, partially  
 850 enveloped by the main foliation, defined by phengite and chloritoid. (b) Detail of the chloritoid inclusions in  
 851 garnet core and mantle. The inset shows a very fine-grained polymineralic inclusion in garnet mantle,  
 852 consisting of glaucophane and jadeite, partially replaced by albite, pyrophyllite and paragonite. (c) Tabular-  
 853 shaped inclusion in garnet mantle, consisting of an aggregate of epidote + paragonite + quartz, possibly  
 854 deriving from former lawsonite. Sample DM1565: (d) Large pre-Alpine garnet porphyroblasts (Grt<sub>1</sub>)  
 855 enveloped by the main foliation. (e) Top: small Alpine garnet idioblasts (Grt<sub>2</sub>) in equilibrium with the main  
 856 foliation defined by phengite; bottom: Grt<sub>2</sub> forming a discontinuous rim around Grt<sub>1</sub>. (f) Large aggregate of



857 fine-grained chloritoid enveloped by the  $S_m$  and interpreted as a pseudomorph after pre-Alpine staurolite.  
858 (a, b, c, d, e: PPL; f and insets in a, d: XPL; inset in b: BSE).

859

860 **Fig. 6** – Garnet compositions plotted in the Prp-Alm-(Grs+Sps) diagram. The zoning trend for each sample is  
861 highlighted by the arrow. Samples are grouped according to their bulk-composition (*i.e.*, Ca-poor vs. Ca-rich  
862 metapelites). For sample DM1565, only compositions of Alpine Grt<sub>2</sub> are plotted.

863

864 **Fig. 7** – Potassic white mica compositions plotted in the Si vs. Fe<sup>2+</sup> + Mg (a.p.f.u.) diagram. Compositions of  
865 micas defining the  $S_m$  are distinguished from those included in garnet and from the late flakes overgrowing  
866 the  $S_m$ . Samples are grouped according to their bulk-composition (*i.e.*, oxidized vs. not oxidized). The dashed  
867 line represents the ideal celadonitic substitution. Note that point analyses for samples DM1485 (PU),  
868 DM1667c (SCU) and DM1504 (RSU) plot slightly above the line of ideal celadonite substitution, thus  
869 suggesting that these white micas contain some Fe<sup>3+</sup>.

870

871 **Fig. 8** – P-T pseudosections modeled for sample DM1485 (PU) using the measured bulk-composition (a), and  
872 the effective bulk-compositions after fractionation of garnet core (b) and of garnet core + mantle (c). Dotted  
873 lines are Rt and Ilm -in/out curves; dashed line is the Qz/Coe transition. The black ellipses show the P-T  
874 conditions constrained for the growth of garnet core (a), mantle (b) and rim (c), based on the intersection of  
875 compositional isopleths, as indicated in each legend. Dark grey squares with dotted ellipses in (c) represent  
876 peak P-T conditions (with 1 $\sigma$  error) as defined by AvPT applied on four different sets of mineral compositions  
877 (see Table 2).

878

879 **Fig. 9** – P-T pseudosections modeled for sample DM1667c (SCU). (a), (b), (c) and all the symbols as in Fig. 8.

880

881 **Fig. 10** – P-T pseudosections modeled for sample DM1281 (BIU). (a), (b), (c) and all the symbols as in Fig. 8;  
882 the inset in (b) clarifies the mineral assemblages stable in the narrow fields modelled in the central part of  
883 the pseudosection. Note that the scale is different from that in Fig. 8, 9 and 11, that pseudosection in (c) has  
884 been calculated at  $a_{H_2O}=0.4$ , and that AvPT data in (b) refer to late prograde P-T conditions.

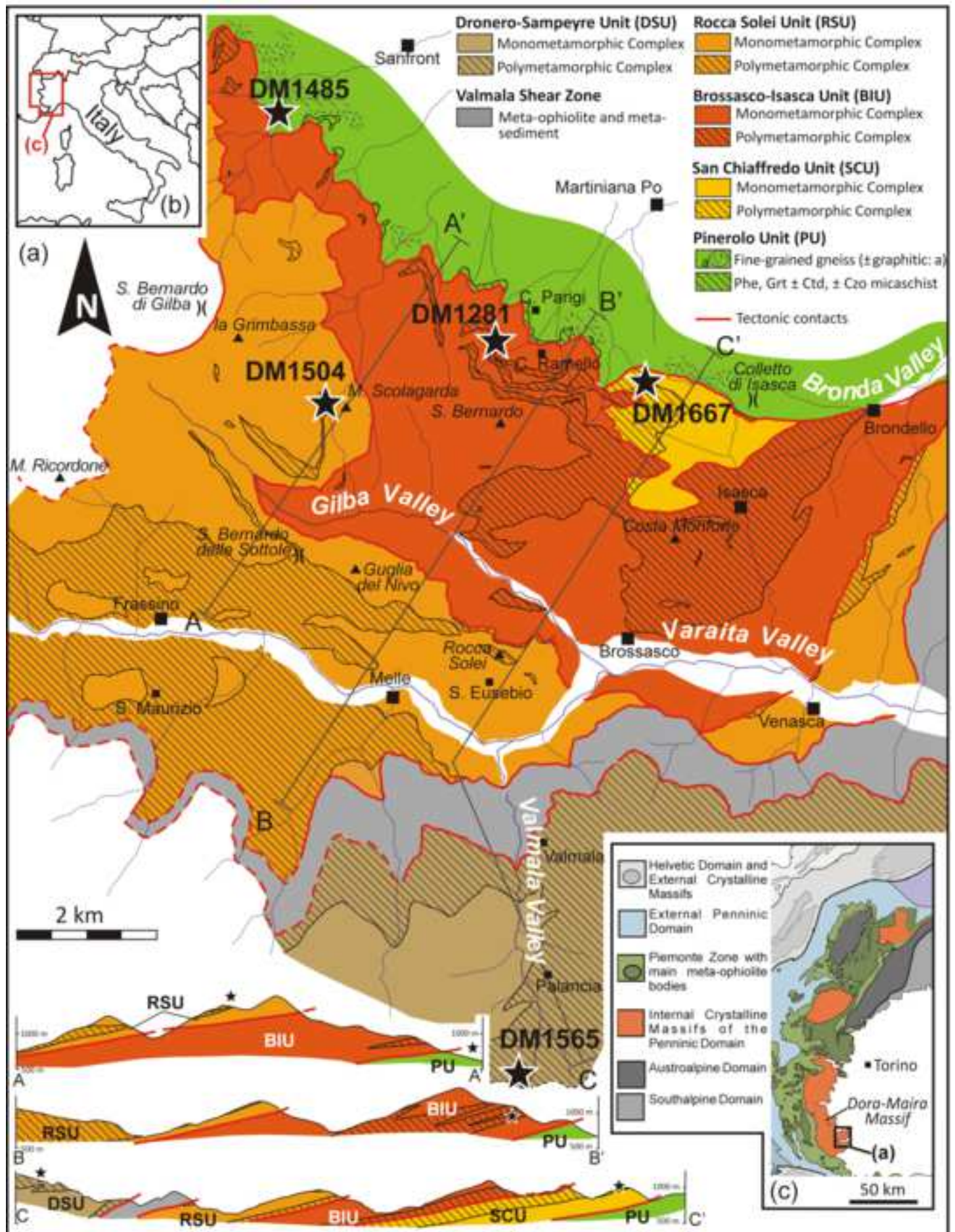
885

886 **Fig. 11** – P-T pseudosections modeled for sample DM1504 (RSU). (a), (b), (c) and all the symbols as in Fig. 8.

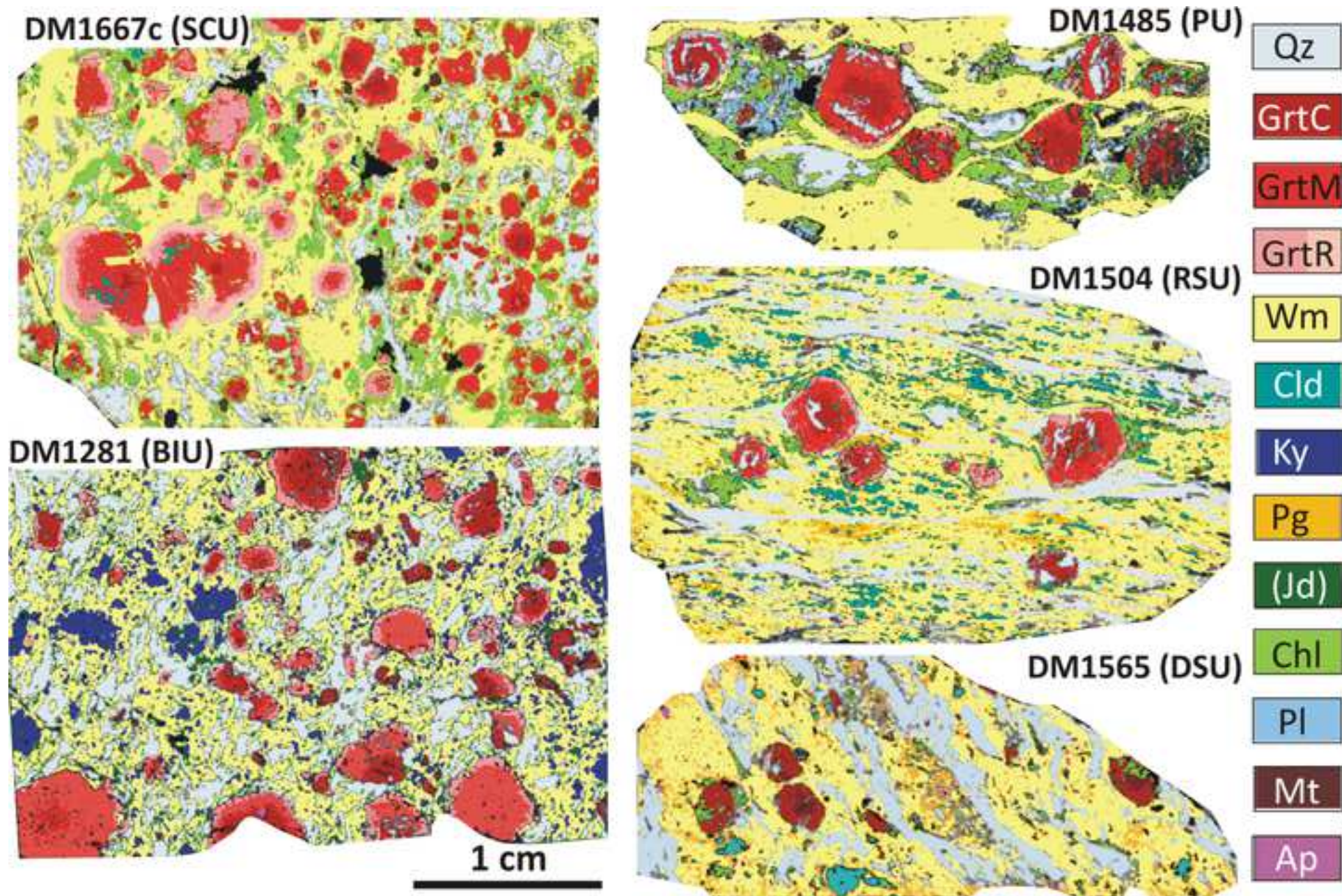
887

888 **Fig. 12** – (a-e) P-T grids showing the prograde trajectories for the Pinerolo Unit (a), San Chiaffredo Unit (b),  
889 Brossasco-Isasca Unit (c), Rocca Solei Unit (d) and Dronero-Sampeyre Unit (e) as inferred in this study,  
890 compared to peak P-T conditions derived from the literature (PU: Avigad *et al.*, 2003; SCU: Compagnoni &  
891 Rolfo, 2003; BIU: Ferrando *et al.*, 2017 and references therein; RSU: Chopin *et al.*, 1991; Matsumoto &  
892 Hirajima, 2000; DSU: Chopin *et al.*, 1991). For the BIU, the prograde and retrograde P-T path inferred from  
893 the literature is also reported. KFMASH reactions relevant for the discussion are reported in (c) (from White  
894 *et al.*, 2014). Note that the BIU retrograde trajectory crosses the Grt + Ky + Chl = St reaction (see Section 6.1.2  
895 for further discussion). (f) Comparison of the prograde P-T trajectories inferred for all the studied units: note  
896 that the early prograde path of the BIU is similar to the P-T trajectory of the other units. Metamorphic facies  
897 are from Liou & Zhang, 2002. The chloritoid stability field, as derived from pseudosections of Fig. 8-11, is  
898 reported in greenish-blue.

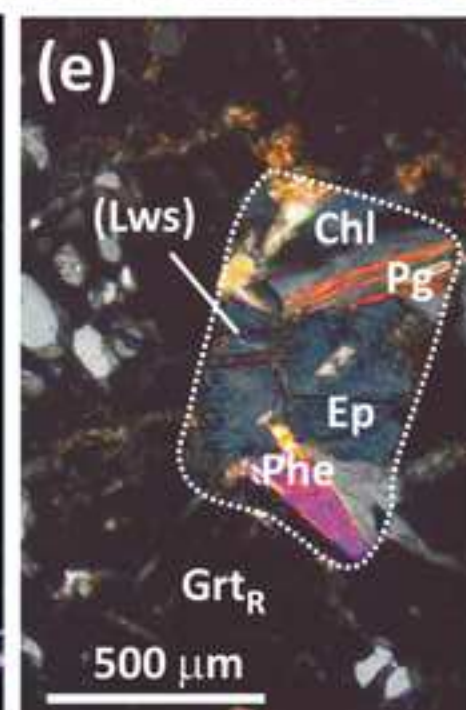
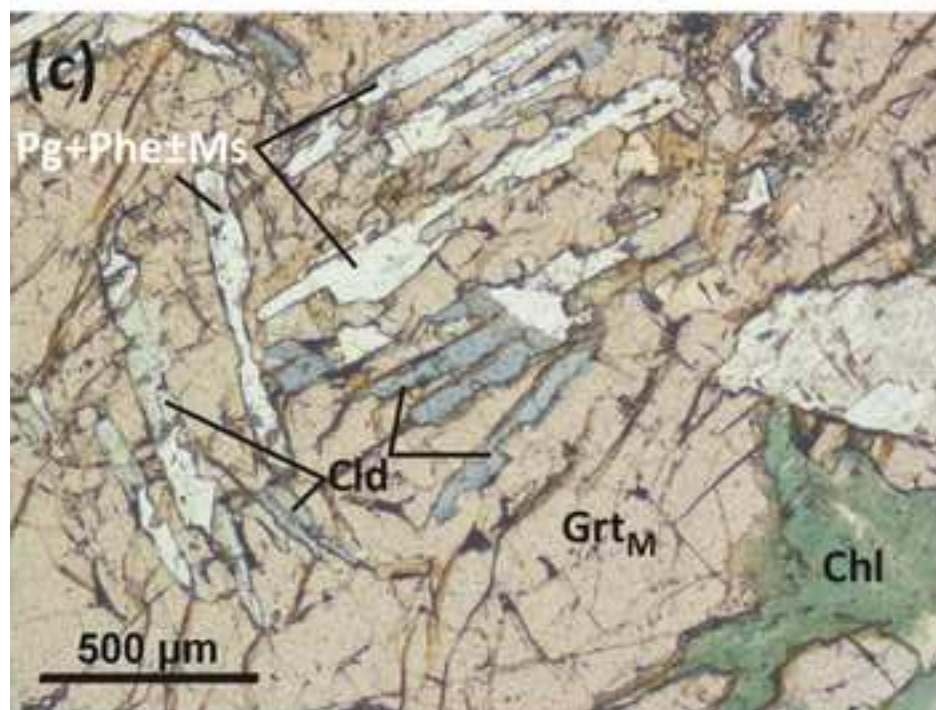
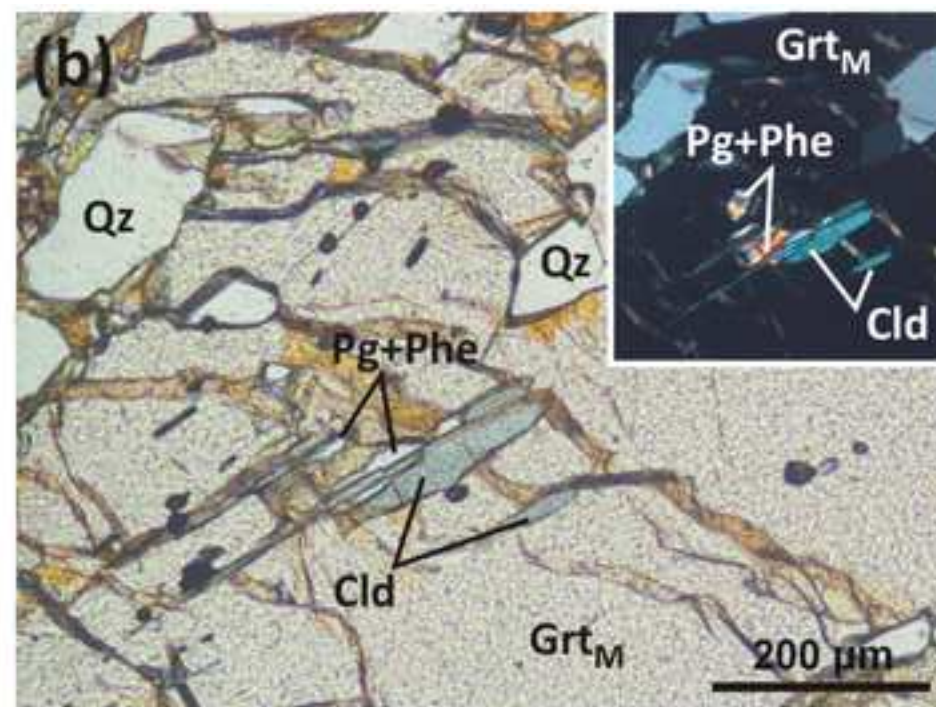
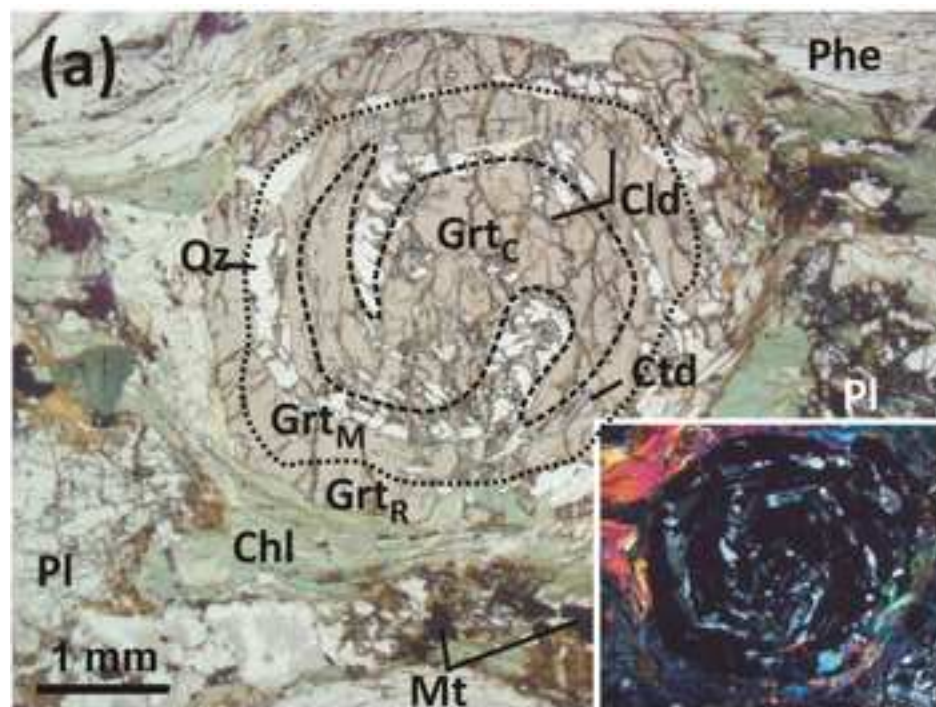
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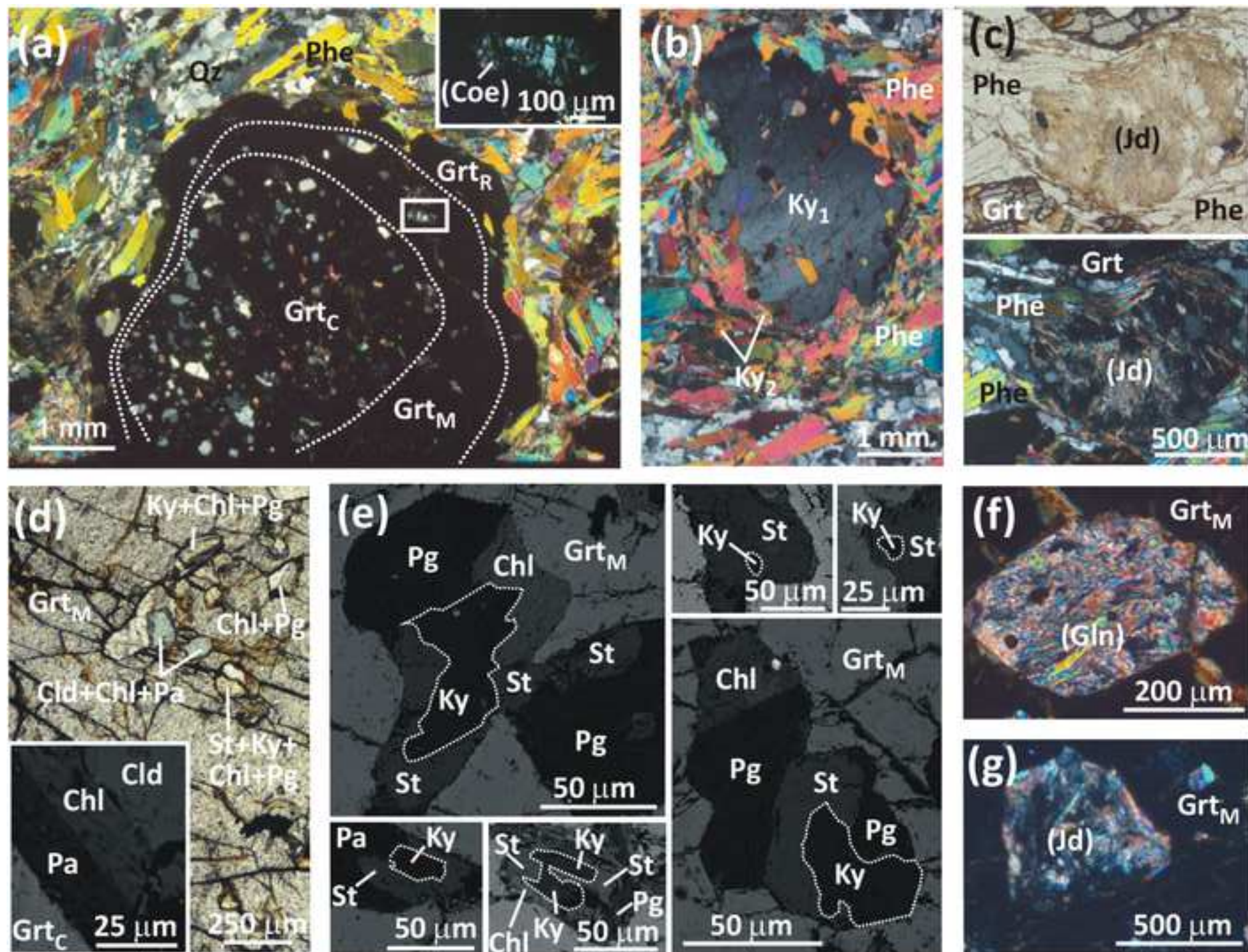
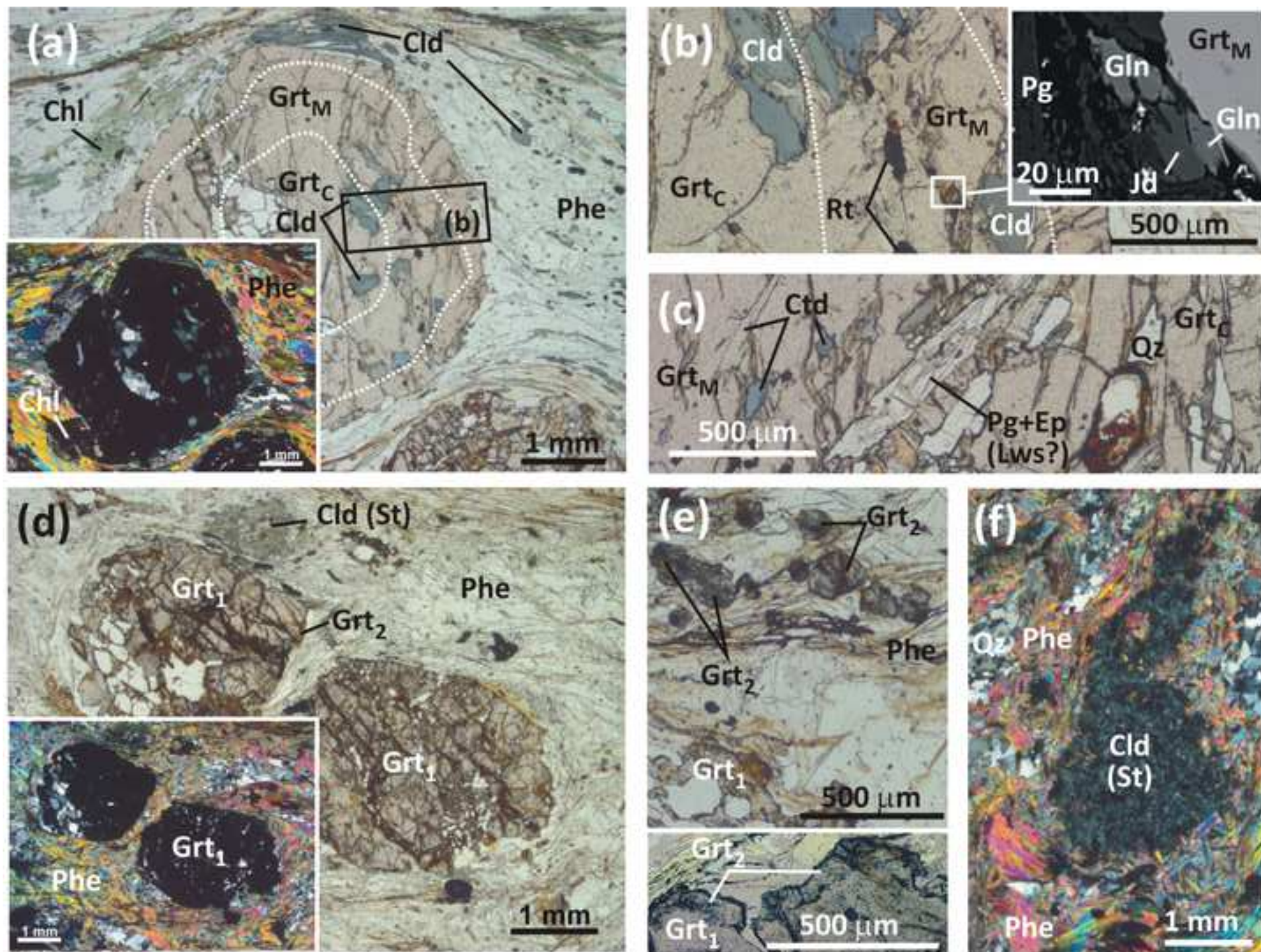




Fig. 5





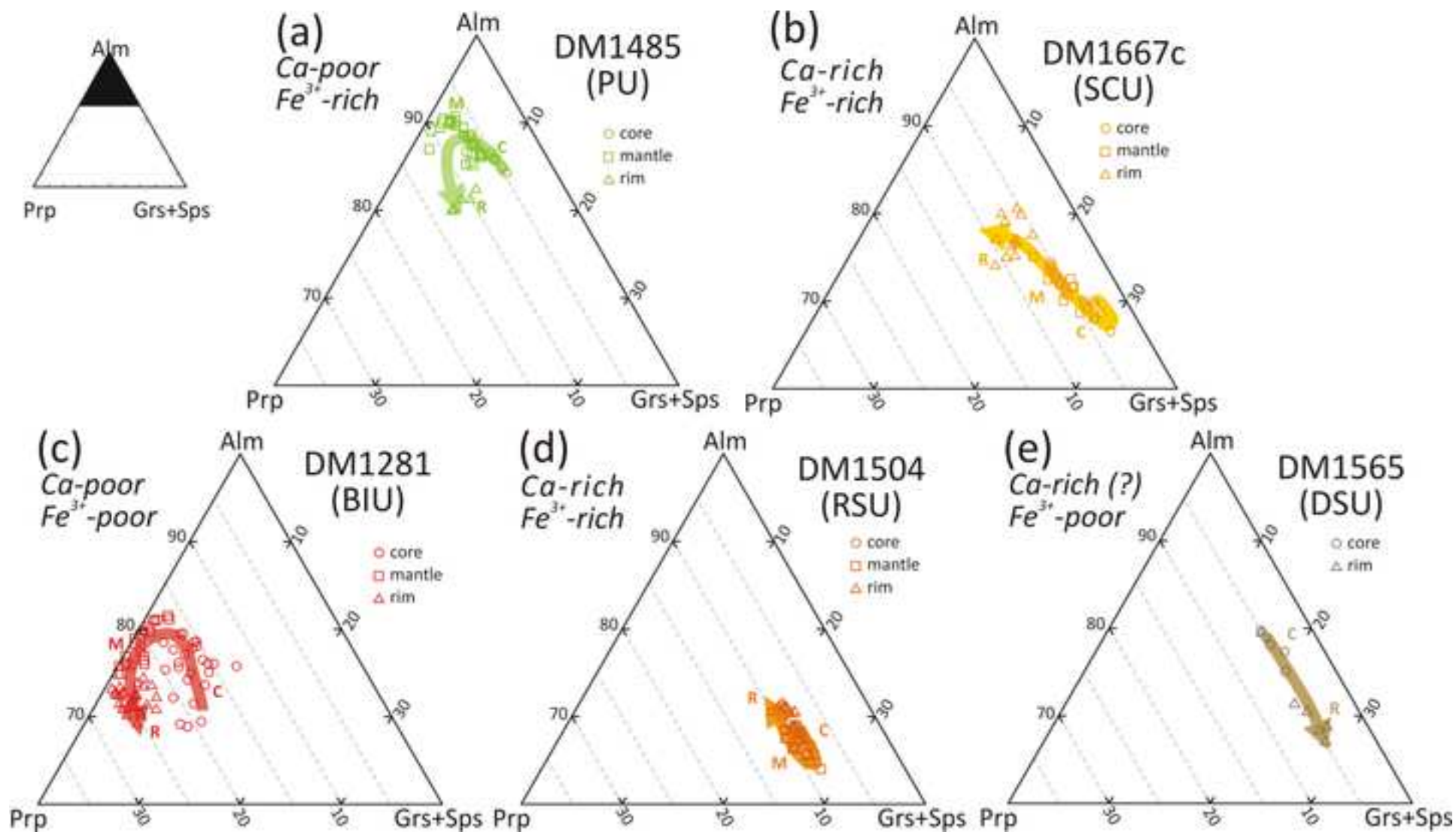
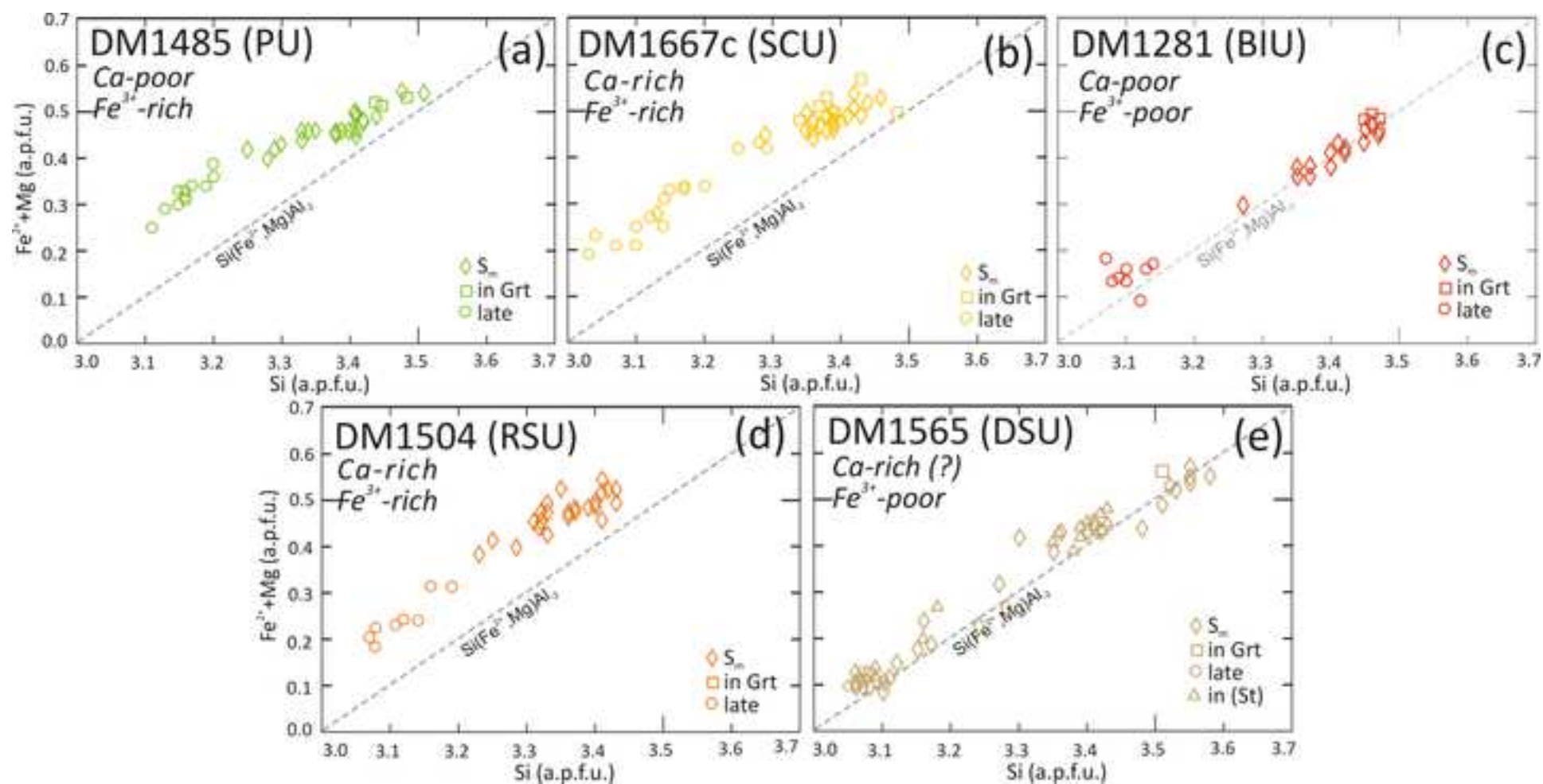
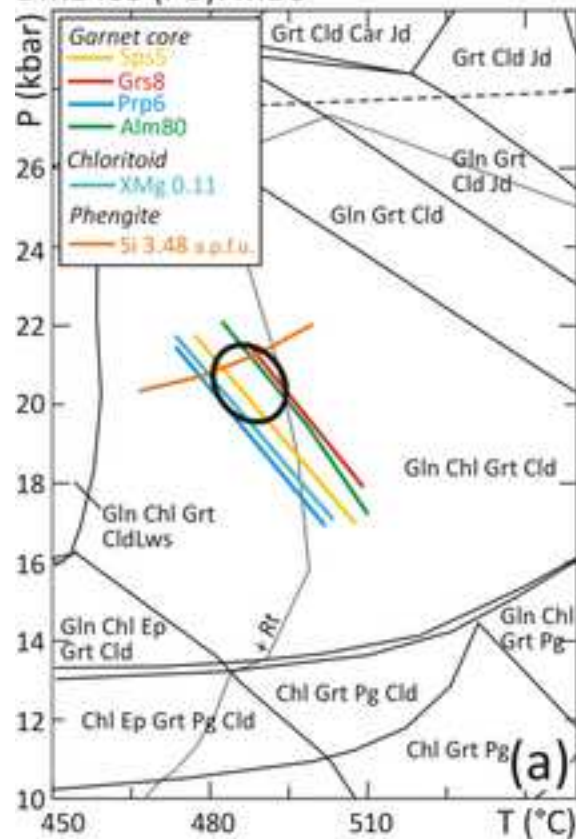
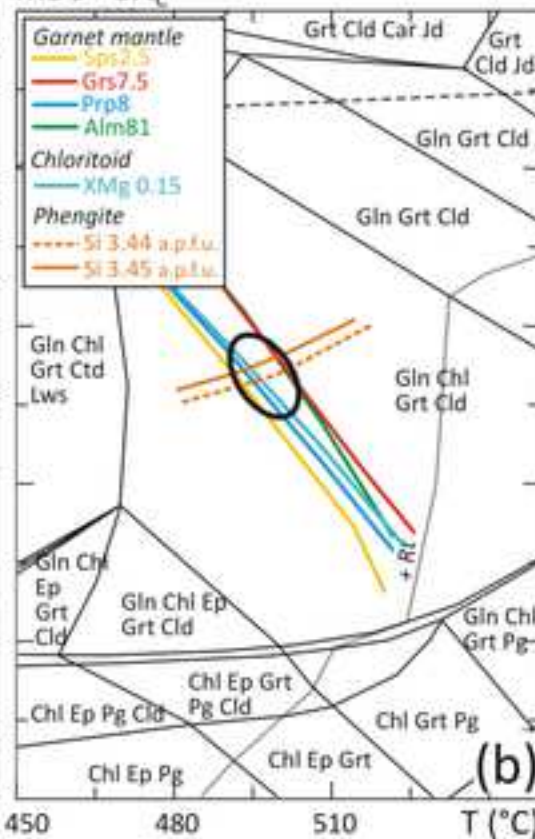
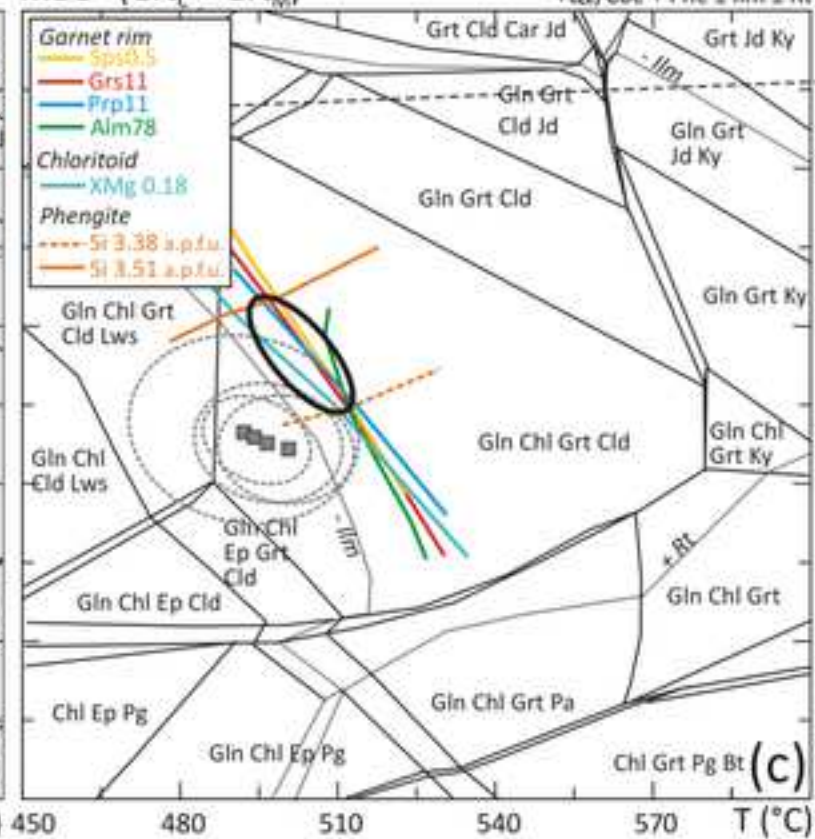


Fig. 7

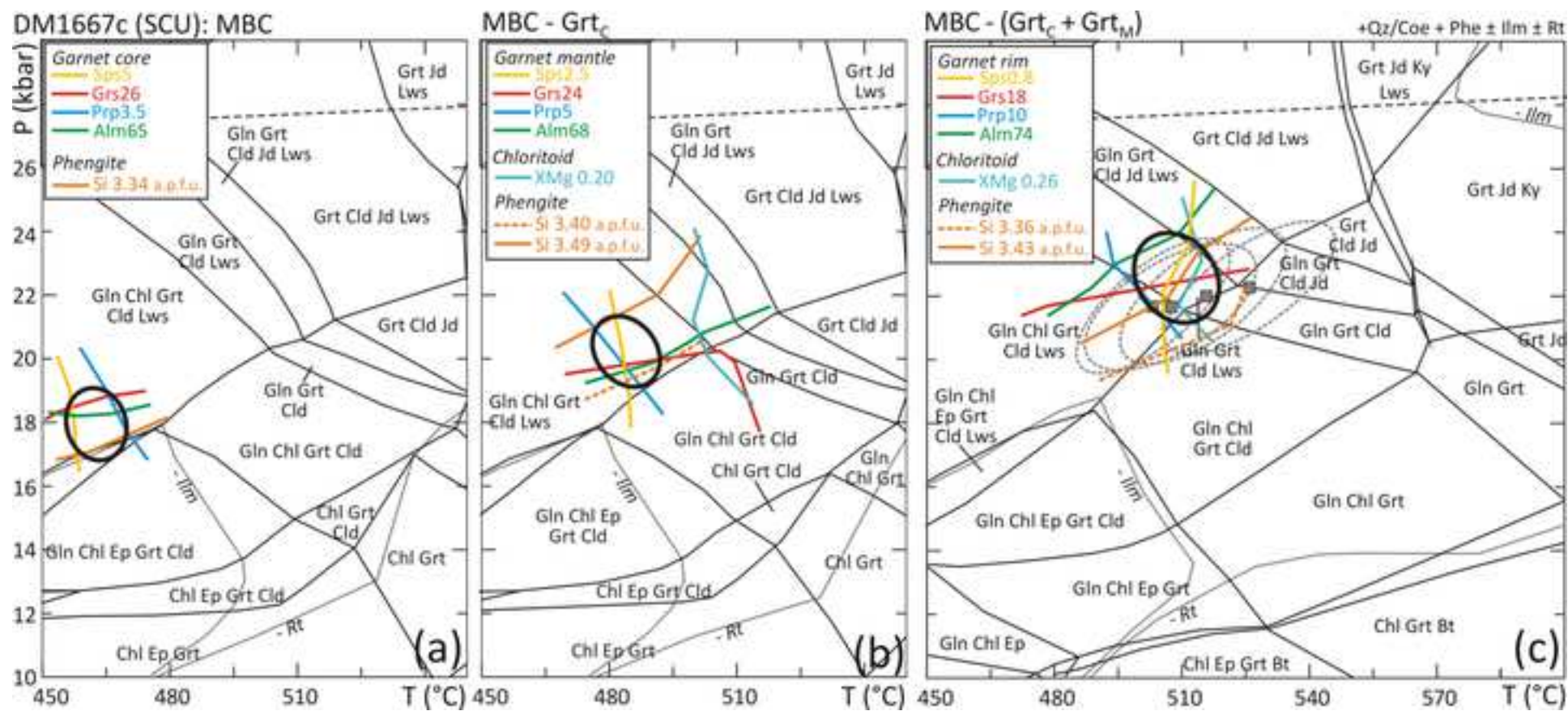




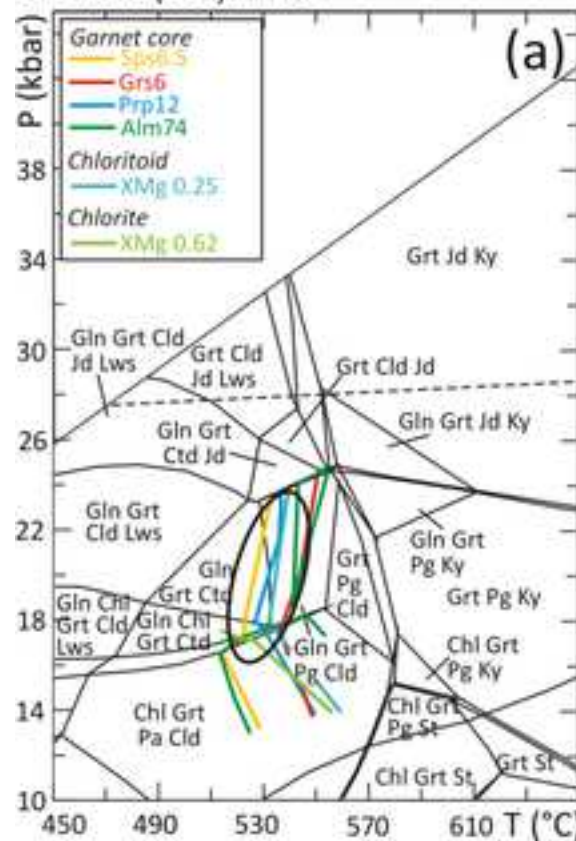
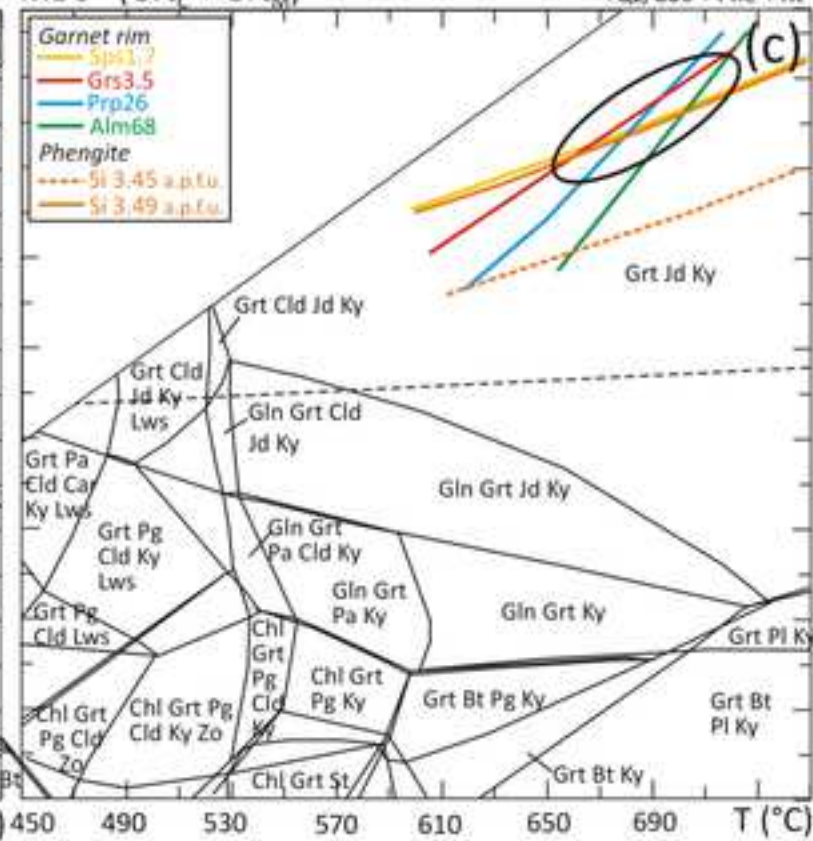
## DM1485 (PU): MBC

MBC - Grt<sub>C</sub>MBC - (Grt<sub>C</sub> + Grt<sub>M</sub>)

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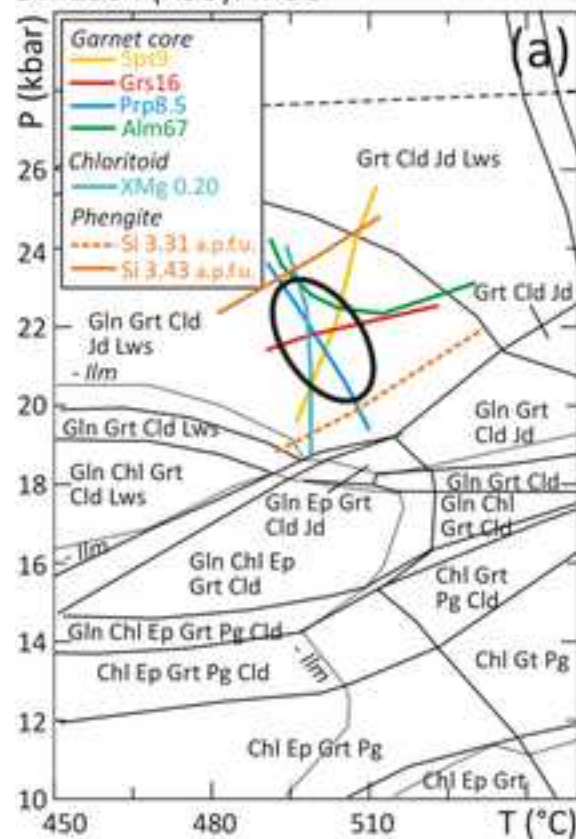
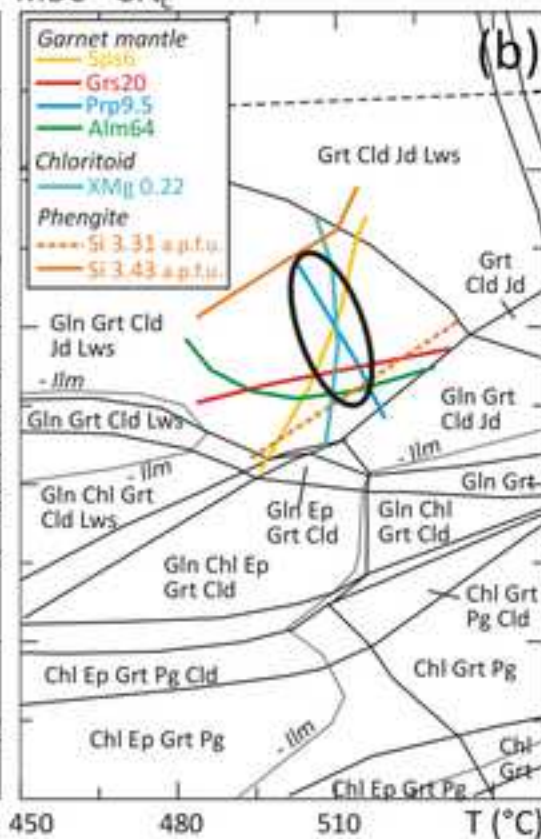
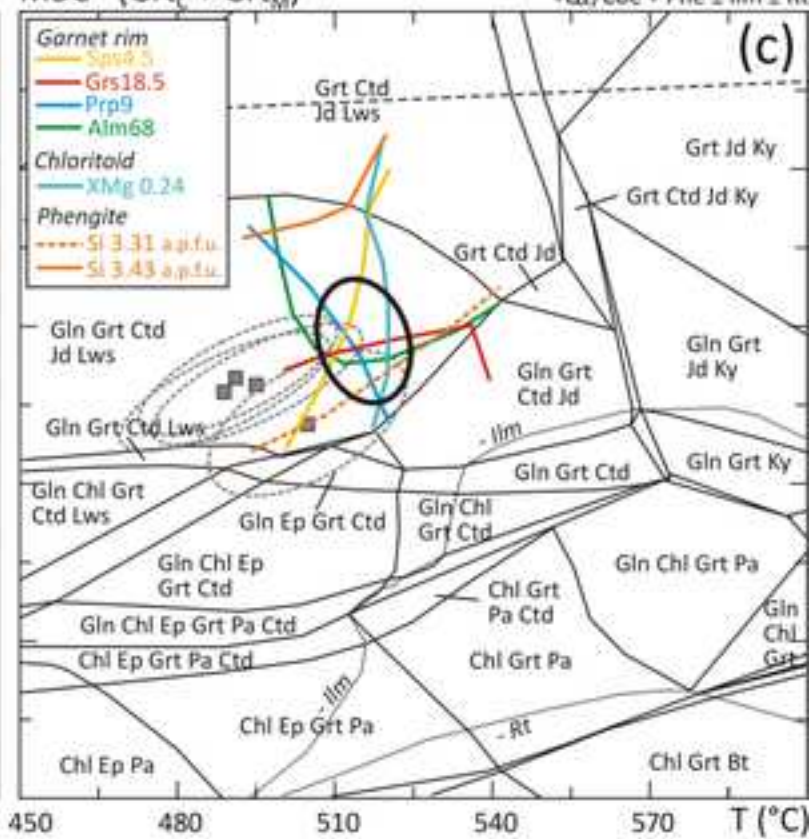


DM1281 (BIU): MBC

MBC - Grt<sub>C</sub>MBC - (Grt<sub>C</sub> + Grt<sub>M</sub>)



DM1504 (RSU): MBC

MBC - Grt<sub>C</sub>MBC - (Grt<sub>C</sub> + Grt<sub>M</sub>)

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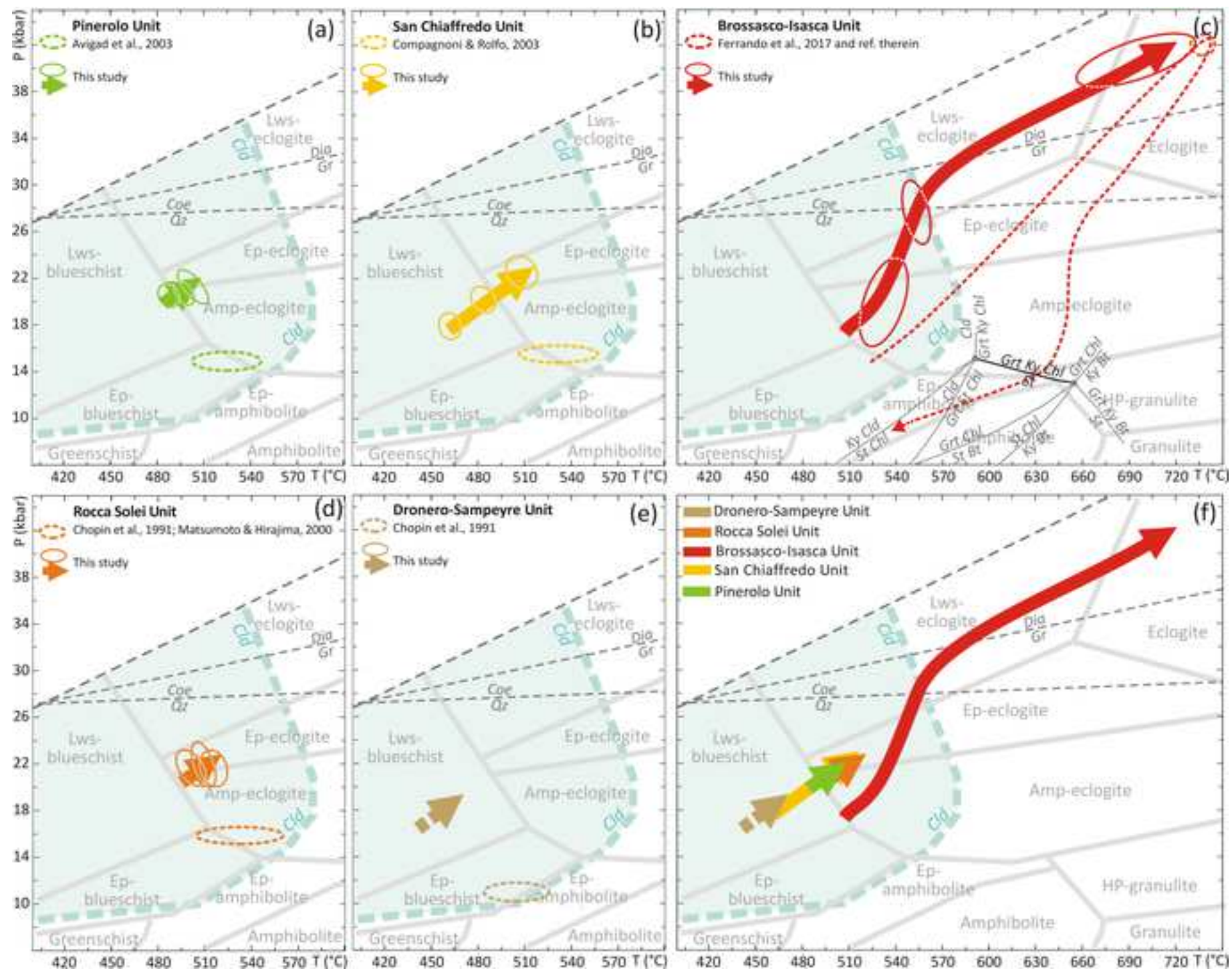


Table 1. Effective bulk-compositions (mol%) of the studied metapelites

Sample	DM1485 (PU)			DM1667c (SCU)			DM1281 (BIU)			DM1504 (RSU)		
	MBC	MBC-Gr <sub>tC</sub>	MBC-(Gr <sub>tC</sub> +Gr <sub>tR</sub> )	MBC	MBC-Gr <sub>tC</sub>	MBC-(Gr <sub>tC</sub> +Gr <sub>tR</sub> )	MBC	MBC-Gr <sub>tC</sub>	MBC-(Gr <sub>tC</sub> +Gr <sub>tR</sub> )	MBC	MBC-Gr <sub>tC</sub>	MBC-(Gr <sub>tC</sub> +Gr <sub>tR</sub> )
SiO <sub>2</sub>	55.61	57.29	59.45	58.38	58.81	64.62	64.40	67.37	71.83	62.46	62.40	63.89
TiO <sub>2</sub>	0.21	0.24	0.27	0.23	0.24	0.32	0.59	0.67	0.79	0.70	0.71	0.76
Al <sub>2</sub> O <sub>3</sub>	14.99	15.11	15.27	14.20	14.16	14.10	16.57	16.89	17.36	17.24	17.19	17.41
Fe <sub>2</sub> O <sub>3</sub>	1.07	0.92	0.73	0.94	0.92	0.61	0.00	0.00	0.00	0.53	0.51	0.43
FeO	16.67	14.50	11.42	14.74	14.45	9.60	9.84	6.71	2.01	7.84	8.07	6.78
MnO	0.38	0.12	0.02	0.33	0.27	0.06	0.29	0.09	0.02	0.28	0.23	0.05
MgO	6.99	7.54	8.12	4.03	4.09	4.80	4.23	3.93	3.00	4.20	4.19	4.21
CaO	0.76	0.56	0.46	4.27	4.09	1.84	0.49	0.26	0.15	1.68	1.60	0.98
Na <sub>2</sub> O	0.68	0.77	0.88	0.32	0.33	0.45	0.75	0.85	1.00	0.90	0.91	0.98
K <sub>2</sub> O	2.64	2.96	3.38	2.57	2.64	3.59	2.84	3.23	3.82	4.15	4.19	4.50

MBC = measured bulk-composition; MBC-Gr<sub>tC</sub> = effective bulk-composition after fractionation of Gr<sub>tC</sub>; MBC-(Gr<sub>tC</sub>+Gr<sub>tM</sub>) = effective bulk-composition after fractionation of Gr<sub>tC</sub> and Gr<sub>tM</sub>.

Table 2

Table 2. Average P-T estimates for the peak (DM1485, DM1667c, DM1504, DM1565) and late prograde (DM1281) assemblages of the studied samples

Sample	Assemblage (+Qz/Coe* + H <sub>2</sub> O)	Phe a.p.f.u.	Si XMg	Grt XMg	Ctd XMg	Chl XMg	average T (°C)	error (σ) T (°C)	average P (kbar)	error (σ) P (kbar)	σfit	N° of reactions
DM1485 (PU)	Phe(6.1)-Grt(1.22)-Ctd(1.49)-Chl(4.7)	3.51	0.12	0.17	0.40		496	15	19	1.5	1.32	4
	Phe(2.31)-Grt(1.2)-Ctd(1.48)-Chl(4.8)	3.48	0.10	0.16	0.40		494	11	19.1	1.1	0.81	4
	Phe(6.11)-Grt(1.21)-Ctd(2.29)-Chl(4.9)	3.44	0.12	0.16	0.40		500	14	18.8	1.4	1.30	5
	Phe(6.6)-Grt(1.23)-Ctd(1.33)-Chl(3.7)	3.42	0.15	0.16	0.44		492	24	19.3	2.5	2.27	5
	<i>weighted mean**</i>						496	7	19.0	0.7		
DM1667c (SCU)	Phe(7.17)-Grt(2.24)-Ctd(1.5)-Lws	3.46	0.08	0.28			526	16	22.3	1.7	0.78	4
	Phe(10.1)-Grt(9.22)-Ctd(2.52)-Lws	3.44	0.09	0.23			503	15	21.7	1.7	0.27	4
	Phe(10.9)-Grt(2.25)-Ctd(2.49)-Lws	3.44	0.10	0.23			515	16	22.0	1.8	0.76	3
	Phe(1.18)-Grt(9.1)-Ctd(2.40)-Lws	3.43	0.08	0.22			507	16	21.7	1.7	0.25	3
	<i>weighted mean**</i>						512	8	21.9	0.9		
DM1281 (BIU)	Phe(12.2)-Grt(6.3)-Ctd(5.7)-Ky	3.47	0.24	0.31			560	9	27.5	2.9	1.03	3
	Phe(12.1)-Grt(6b.1)-Ctd(6.49)-Ky	3.45	0.25	0.30			552	9	26.3	2.7	0.43	3
	Phe(6.88)-Grt(6.32)-Ctd(6.36)-Ky	3.45	0.24	0.31			561	10	25.2	3.1	1.09	3
	Phe(8.3)-Grt(10.13)-Ctd(6.33)-Ky	3.46	0.24	0.29			557	9	27.5	0.4	0.83	4
	<i>weighted mean**</i>						557	5	27.4	0.4		
DM1504 (RSU)	Phe(2.34)-Grt(2.2)-Ctd(2.35)-Gln(2.52)-Jd(2.44)-Lws	3.42	0.09	0.22			491	15	20.7	1.2	1.24	7
	Phe(6.21)-Grt(2.26)-Ctd(4.4)-Gln(2.52)-Jd(2.44)-Lws	3.43	0.10	0.23			505	16	19.5	1.6	1.22	5
	Phe(6.16)-Grt(1.19)-Ctd(6.8)-Gln(2.52)-Jd(2.44)-Lws	3.41	0.09	0.23			489	16	20.3	1.2	1.30	6
	Phe(6.3)-Grt(2.1)-Ctd(2.32)-Gln(2.52)-Jd(2.44)-Lws	3.43	0.09	0.23			495	16	20.5	1.2	1.31	7
	<i>weighted mean**</i>						495	8	20.3	0.6		
DM1565 (DSU)	Phe(5.12)-Grt(3.15)-Ctd(2.3)-Lws	3.55	0.06	0.17			466	14	18.8	1.5	0.15	3
	Phe(5.6)-Grt(3.11)-Ctd(2.32)-Lws	3.55	0.05	0.18			446	14	16.4	1.3	0.29	3
	Phe(3.6)-Grt(7.1)-Ctd(2.25)-Lws	3.58	0.05	0.15			444	14	16.8	1.3	0.55	3
	<i>weighted mean**</i>						452	8	17.2	0.8		

\*Coe for sample DM1281

\*\*Weighted mean (with error) implies that values with smaller errors weight more than values with bigger errors.

## What's in the sandwich? New P-T constraints for the (U)HP nappe stack of southern Dora-Maira Massif (Western Alps)

submitted to *European Journal of Mineralogy* (Ref: ejm190006) by

Chiara Groppo, Simona Ferrando, Manuele Gilio, Serena Botta, Francesco Nosenzo, Gianni Balestro, Andrea Festa, Franco Rolfo

### SUPPLEMENTARY MATERIAL

#### Sample locations

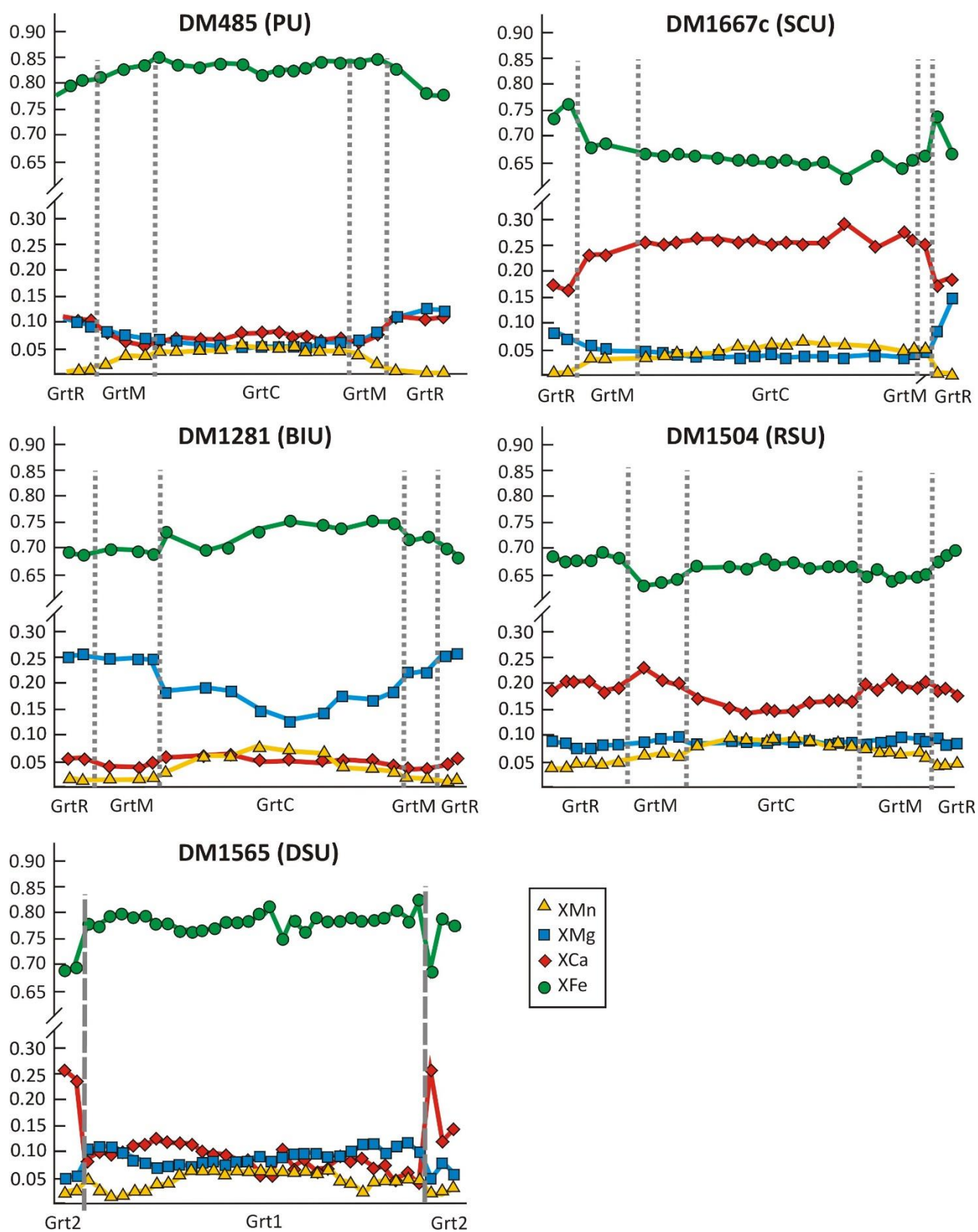
The five metapelite samples studied in this paper are part of the rich collection of thin sections from the southern DMM hosted at the Department of Earth Sciences of the University of Torino (Italy). Sample locations are reported in Fig. 1 and additional details are given below.

- **Sample DM1485 (PU)** was collected from a small (few metres) outcrop of garnet-bearing micaschists exposed at Case dei Canaveis, in the Comba Albetta valley (right tributary of the Po river, west of Sanfront).
- **Sample DM1667c (SCU)** was collected at Piano Pramalano, at the head of Isasca Valley (few tens of metres below the ridge separating the Isasca Valley from the Po Valley). Outcrop exposure is very poor and the sample was collected from the debris along the road; however, because the debris is totally composed of similar micaschists, we suppose that this is the dominant lithology of the area.
- **Sample DM1281 (BIU)** was collected from an outcrop located east of Piano la Ruota, at the head of the Rio Lavesio Valley (a right tributary of the Po river, south-west of Martiniana Po; the same small valley where there is the well-known locality of Case Parigi). The outcrop consists of a ten of metres thick level of metapelites hosted within augen-gneiss. A sample from the same outcrop was described by Compagnoni *et al.* (1994) in the guidebook for the field excursion organized for the 16<sup>th</sup> meeting of IMA.
- **Sample DM1504 (RSU)** was collected from a 20-50 m -thick layer of metapelites exposed on the ridge separating the Gilba Valley from the Po Valley, west of M. Scolagarda.
- **Sample DM1565 (DSU)** was collected close to the Santuario di Valmala at the head of the Valmala Valley, few hundred metres below the ridge between the Varaita and Maira Valleys. Henry (1990) described similar micaschists exposed south of Meira Palancia as “micaschistes amigdalaires” and reported the occurrence of relics of pre-Alpine staurolite only partially replaced by a fine-grained aggregate of chloritoid.

Compagnoni, R., Messiga, B., Castelli, D. (1994): High pressure metamorphism in the Western Alps. *in*: “Guidebook to the field excursion B1”, 16th General Meeting of the International Mineralogical Association, Pisa, Italy, 148 pp.

Henry, C. (1990): L'unité à coesite du massif Dora-Maira dans son cadre pétrologique et structurale (Alpes Occidentales, Italie). Thèse Doctorat., Université Paris 6, 149 pp.





**Fig. SM1** – Compositional profiles of garnet porphyroblasts from the investigated samples.

**Table SM1a - Compositional variations of the main minerals in samples DM1485 (PU), DM1667c (SCU) and DM1281 (BIU)**

DM1485 (PU)				
<i>Garnet</i>	Sps	Prp	Grs	Alm
GrtC	4-6	5-7	7-9	80-83
GrtM	2-3	7-9	7-8	81-84
GrtR	0.3-1	9-12	10-11	77-81
<hr/>				
<i>Phengite</i>	Si (a.p.f.u.)			
Sm	3.38-3.51			
in GrtC	3.48			
in GrtM	3.44-3.45			
<hr/>				
<i>Chloritoid</i>	XMg			
in GrtC	0.10-0.12			
in GrtM	0.13-0.16			
in GrtR	0.17-0.18			
<hr/>				
<i>Chlorite</i>	XMg			
Sm	0.40-0.44			
late	0.37-0.38			
<hr/>				
<i>Biotite</i>	XMg			
late	0.38-0.40			

DM1667c (SCU)				
<i>Garnet</i>	Sps	Prp	Grs	Alm
GrtC	4-7	3-4	25-27	64-66
GrtM	2-3	4-6	18-19	73-75
GrtR	0.5-1	7-10	16-20	72-76
GrtO-R	1-2	5-7	18-19	73-75
<hr/>				
<i>Phengite</i>	Si (a.p.f.u.)			
Sm	3.35-3.46			
in GrtC	3.34			
in GrtM	3.40-3.49			
in GrtR	3.36-3.43			
<hr/>				
<i>Chloritoid</i>	XMg			
in GrtC/M	0.20-0.28			
in GrtR	0.25-0.28			
<hr/>				
<i>Chlorite</i>	XMg			
in GrtC/M	0.20-0.26			
late	0.37-0.42			
<hr/>				
<i>Epidote</i>	XPs			
in GrtC/M	0.50-0.84			
late	0.32-0.46			
<hr/>				
<i>Biotite</i>	XMg			
late	0.35-0.42			

DM1281 (BIU)				
<i>Garnet</i>	Sps	Prp	Grs	Alm
GrtC	3-8	12-16	5-6	73-77
GrtM	0.5-2	17-21	1-3	74-79
GrtR	1-2	22-26	3-5	68-72
<hr/>				
<i>Phengite</i>	Si (a.p.f.u.)			
Sm	3.35-3.49			
in GrtR	3.45-3.47			
<hr/>				
<i>Chloritoid</i>	XMg			
in GrtC/M	0.25-0.31			
<hr/>				
<i>Chlorite</i>	XMg			
in GrtM	0.59-0.66			
in GrtC	0.33-0.50			
<hr/>				
<i>Staurolite</i>	XMg			
in GrtC/M	0.15-0.25			

**Table SM1b - Compositional variations of the main minerals in samples DM1504 (RSU) and DM1565 (DSU)**

DM1504 (RSU)				
Garnet	Sps	Prp	Grs	Alm
GrtC	7-10	8-9	14-18	66-69
GrtM	5-7	9-10	19-21	63-65
GrtR	4-5	8-10	17-20	66-70
Phengite	Si (a.p.f.u.)			
Sm	3.31-3.43			
Chloritoid	XMg			
Sm CtdC	0.19-0.21			
Sm CtdR	0.22-0.24			
in GrtC	0.19-0.21			
in GrtM	0.21-0.23			
in GrtR	0.22-0.24			
Glaucophane	XMg		XNa	
in GrtM/R	0.38-0.42		0.91-0.94	
Jadeite	XJd		XAeg	
in GrtM/R	0.66-0.74		0.26-0.34	
Epidote	XPs			
late (in Grt)	0.53-0.63			
late (matrix)	0.55-0.71			
Chlorite	XMg			
late	0.42-0.47			

DM1565 (DSU)				
Garnet 1	Sps	Prp	Grs	Alm
GrtC	3-7	6-9	5-10	75-80
GrtM	1-2	9.11	9-12	78-80
GrtR	2-5	10-12	4-9	78-82
Garnet 2	Sps	Prp	Grs	Alm
GrtC	2-4	4-5	14-16	75-78
GrtR	2-3	5-6	21-26	67-72
Phengite	Si (a.p.f.u.)			
Sm	3.48-3.58			
Chloritoid	XMg			
Sm; after St	0.13-0.18			
Chlorite	XMg			
late	0.40-0.44			

**Table SM2a - Representative analyses of the main minerals in sample DM1485 (PU)**

Analysis	White mica								Garnet					
	1.39 Phe	1.35 Phe	6.1 Phe*	2.31 Phe*	6.11 Phe*	6.6 Phe*	4.6 Ms	1.43 Pg	1.12 Grt	1.19 Grt	1.22 Grt*	1.2 Grt*	1.21 Grt*	1.23 Grt*
Site	In Grt <sub>C</sub>	In Grt <sub>M</sub>	// S <sub>m</sub>	// S <sub>m</sub>	// S <sub>m</sub>	// S <sub>m</sub>	late	In Grt <sub>M</sub>	Core	Mantle	Rim	Rim	Rim	Rim
SiO <sub>2</sub>	52.86	52.32	53.71	53.42	52.51	52.01	47.63	47.30	36.55	36.41	36.79	36.77	37.04	37.53
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	26.37	27.19	26.21	26.76	27.49	27.84	32.96	39.85	20.36	20.27	20.77	20.65	20.96	21.01
FeO	4.65	4.75	2.96	2.86	3.26	2.55	3.88	0.96	36.66	36.95	35.00	35.54	35.21	31.73
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.17	0.99	0.07	0.36	0.08	0.11
MgO	2.74	2.69	3.93	3.88	3.20	3.50	1.16	0.00	1.18	1.85	2.91	2.42	3.03	3.69
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.68	2.49	3.71	3.48	3.47	5.78
Na <sub>2</sub> O	0.66	0.70	0.00	0.00	0.61	0.85	1.32	8.07	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	9.15	9.18	9.90	9.98	9.54	9.39	9.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.43	96.83	96.72	96.89	96.61	96.15	96.11	96.21	99.67	99.06	99.36	99.29	99.88	99.95
Si	3.48	3.44	3.51	3.48	3.44	3.42	3.16	2.99	2.99	2.99	2.98	2.99	2.98	2.98
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	2.05	2.11	2.02	2.06	2.12	2.16	2.58	2.97	1.97	1.96	1.98	1.98	1.99	1.97
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.06	0.07	0.05	0.06	0.06
Fe <sup>+2</sup>	0.26	0.26	0.16	0.16	0.18	0.14	0.22	0.03	2.47	2.47	2.30	2.37	2.31	2.05
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.07	0.00	0.02	0.01	0.01
Mg	0.27	0.26	0.38	0.38	0.31	0.34	0.11	0.00	0.14	0.23	0.35	0.29	0.36	0.44
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.22	0.32	0.30	0.30	0.49
Na	0.08	0.09	0.00	0.00	0.08	0.11	0.17	0.99	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.83	0.83	0.80	0.79	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.51	0.50	0.70	0.71	0.64	0.71	0.35	0.00	0.05	0.08	0.12	0.10	0.12	0.15
XFe									0.82	0.83	0.77	0.79	0.78	0.69
XCa									0.08	0.07	0.11	0.10	0.10	0.17
XMn									0.05	0.02	0.00	0.01	0.00	0.00

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 11 oxygens for white mica and 12 oxygens for garnet.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM2b - Representative analyses of the main minerals in sample DM1485 (PU)**

Analysis Site	Chloritoid						Chlorite			
	1.28 Cld In Grt <sub>C</sub>	1.46 Cld In Grt <sub>M</sub>	1.49 Cld* In Grt <sub>R</sub>	1.48 Cld* In Grt <sub>R</sub>	2.29 Cld* In Grt <sub>R</sub>	1.33 Cld* In Grt <sub>R</sub>	4.7 Chl* // S <sub>m</sub>	4.8 Chl* // S <sub>m</sub>	4.9 Chl* // S <sub>m</sub>	3.7 Chl* // S <sub>m</sub>
SiO <sub>2</sub>	24.60	24.60	24.59	25.10	24.63	24.91	24.60	25.05	24.62	25.45
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	39.72	39.51	39.61	40.40	40.21	40.08	22.03	21.78	21.81	21.82
FeO	27.10	26.47	25.87	25.42	25.40	25.82	30.44	30.65	30.38	28.90
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	1.77	2.38	2.91	2.80	2.79	2.72	11.27	11.39	11.47	12.50
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	93.28	93.1	93.17	93.77	93.13	93.63	88.34	88.87	88.28	88.68
Si	2.04	2.03	2.02	2.05	2.02	2.04	2.65	2.68	2.65	2.71
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	3.87	3.85	3.84	3.88	3.89	3.86	2.80	2.75	2.77	2.74
Fe <sup>+3</sup>	0.06	0.09	0.11	0.03	0.06	0.06	0.00	0.00	0.00	0.00
Fe <sup>+2</sup>	1.82	1.74	1.67	1.71	1.68	1.71	2.74	2.75	2.74	2.57
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.22	0.29	0.36	0.34	0.34	0.33	1.81	1.82	1.84	1.98
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.11	0.14	0.18	0.17	0.17	0.16	0.40	0.40	0.40	0.44

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 14 oxygens for chloritoid and 18 oxygens for chlorite.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM3a - Representative analyses of the main minerals in sample DM1667c (SCU)**

Analysis	White mica								Garnet					
	9.28 Phe	9.29 Phe	7.19 Phe	7.17 Phe*	10.1 Phe*	10.9 Phe*	1.18 Phe*	2.27 Pa	9.11 Grt	9.4 Grt	2.24 Grt*	9.22 Grt*	2.25 Grt*	9.1 Grt*
Site	In Grt <sub>C</sub>	In Grt <sub>M</sub>	In Grt <sub>R</sub>	// S <sub>m</sub>	// S <sub>m</sub>	// S <sub>m</sub>	// S <sub>m</sub>	In Grt <sub>M</sub>	Core	Mantle	Rim	Rim	Rim	Rim
SiO <sub>2</sub>	50.42	53.00	51.56	52.25	52.44	52.22	52.28	47.14	36.70	36.79	37.01	36.82	36.55	37.04
TiO <sub>2</sub>	0.45	0.00	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	28.68	26.56	26.26	26.59	27.00	27.25	27.66	40.04	20.15	20.50	20.73	20.69	20.24	20.57
FeO	3.36	3.52	4.36	3.55	3.41	3.88	3.35	0.63	30.67	31.54	33.16	33.87	32.36	33.46
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.35	1.48	0.49	0.32	0.82	0.34
MgO	2.90	3.15	3.36	3.32	3.40	3.18	3.19	0.00	0.88	1.23	1.95	2.12	2.36	2.07
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	8.81	7.97	6.18	5.80	6.52	5.97
Na <sub>2</sub> O	0.91	0.87	0.56	0.62	0.57	0.00	0.58	7.72	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	9.47	9.00	9.76	9.78	9.98	10.18	9.86	0.21	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.19	96.10	96.24	96.11	96.80	96.71	96.92	96.06	99.55	99.52	99.53	99.62	98.85	99.46
Si	3.34	3.49	3.43	3.46	3.44	3.44	3.43	2.99	2.970	2.974	2.987	2.970	2.964	2.992
Ti	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	2.24	2.06	2.06	2.07	2.09	2.11	2.14	2.99	1.923	1.953	1.972	1.967	1.934	1.959
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.137	0.099	0.054	0.094	0.139	0.057
Fe <sup>+2</sup>	0.19	0.19	0.24	0.20	0.19	0.21	0.18	0.03	1.940	2.034	2.184	2.192	2.056	2.203
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.161	0.102	0.034	0.022	0.056	0.023
Mg	0.29	0.31	0.33	0.33	0.33	0.31	0.31	0.00	0.106	0.149	0.235	0.255	0.285	0.249
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.764	0.690	0.535	0.501	0.567	0.517
Na	0.12	0.11	0.07	0.08	0.07	0.00	0.07	0.95	0.00	0.00	0.00	0.00	0.00	0.00
K	0.80	0.76	0.83	0.83	0.84	0.85	0.82	0.02	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.606	0.615	0.579	0.625	0.64	0.594	0.629	0.00	0.04	0.05	0.08	0.09	0.10	0.08
XFe									0.65	0.68	0.73	0.74	0.69	0.74
XCu									0.26	0.23	0.18	0.17	0.19	0.17
XMn									0.05	0.03	0.01	0.01	0.02	0.01

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 11 oxygens for white mica and 12 oxygens for garnet.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM3b - Representative analyses of the main minerals in sample DM1667c (SCU)**

Analysis Site	Chloritoid				Epidote		Chlorite	
	1.5 Cld*	2.52 Cld*	2.49 Cld*	2.40 Cld*	11.12 Ep	9.27 Ep	1.22 Chl	3.1 Chl
	In Grt <sub>R</sub>	In Grt <sub>M</sub>	In Grt <sub>M</sub>	In Grt <sub>M</sub>	In Grt <sub>C</sub>	In (Lws)	In Grt <sub>C</sub>	late
SiO <sub>2</sub>	25.13	25.35	25.13	25.01	38.47	38.63	23.59	24.66
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	40.92	40.67	40.86	40.67	25.47	29.15	20.32	21.54
FeO	22.61	23.72	23.15	23.55	10.63	6.15	37.03	31.18
MnO	4.82	4.03	3.92	3.74	0.00	0.00	0.55	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	7.01	11.43
CaO	0.00	0.00	0.00	0.00	22.15	23.56	0.00	0.00
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	93.48	93.77	93.05	92.97	96.72	97.49	88.50	88.82
Si	2.02	2.05	2.04	2.04	3.02	2.99	2.64	2.65
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	3.88	3.87	3.91	3.91	2.36	2.65	2.68	2.72
Fe <sup>+3</sup>	0.08	0.04	0.01	0.02	0.70	0.40	0.04	0.00
Fe <sup>+2</sup>	1.44	1.56	1.57	1.58	0.00	0.00	3.42	2.80
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Mg	0.58	0.49	0.47	0.45	0.00	0.00	1.17	1.83
Ca	0.00	0.00	0.00	0.00	1.86	1.95	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.28	0.23	0.23	0.22			0.25	0.40
XP <sub>s</sub>					0.64	0.36		

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 14 oxygens for chloritoid, 12 oxygens for epidote and 18 oxygens for chlorite.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM4a - Representative analyses of the main minerals in sample DM1281 (BIU)**

Analysis Site	White mica							Garnet					
	12.2Phe* // S <sub>m</sub>	12.1 Phe* // S <sub>m</sub>	6.88 Phe* // S <sub>m</sub>	8.3 Phe* // S <sub>m</sub>	9.23 Phe In Grt <sub>R</sub>	10.20 Ms In Grt <sub>C</sub>	6.51 Pa In Grt <sub>C</sub>	Grt 11.10 Core	6.3 Grt* Mantle	6b.1 Grt* Mantle	6.32 Grt* Mantle	10.13Grt* Mantle	6.1 Grt Rim
SiO <sub>2</sub>	53.17	52.77	52.96	53.02	53.11	47.77	47.39	37.07	37.28	37.86	37.43	37.71	37.85
TiO <sub>2</sub>	0.40	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	27.15	27.20	28.20	27.27	27.23	36.21	40.38	21.08	21.33	21.40	21.22	21.37	21.67
FeO	1.65	1.72	1.48	1.77	1.81	1.48	0.00	33.55	33.98	31.76	33.77	33.72	32.23
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.21	0.08	0.64	0.23	0.20	0.53
MgO	3.77	3.82	3.64	3.81	3.92	0.81	0.60	3.09	5.93	6.23	6.12	6.07	6.57
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.79	0.43	1.63	0.31	0.59	0.98
Na <sub>2</sub> O	0.00	0.00	0.00	0.51	0.66	2.11	7.35	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	10.34	10.52	10.32	10.38	9.42	8.20	0.40	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.48	96.50	96.60	96.75	96.16	96.58	96.13	99.79	99.03	99.52	99.07	99.66	99.82
Si	3.47	3.45	3.45	3.46	3.47	3.10	3.01	2.99	2.977	2.992	2.985	2.988	2.980
Ti	0.02	0.02	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00
Al	2.09	2.10	2.16	2.10	2.10	2.77	3.02	2.00	2.007	1.993	1.995	1.9957	2.010
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.040	0.022	0.036	0.0282	0.031
Fe <sup>+2</sup>	0.09	0.09	0.08	0.10	0.10	0.08	0.03	2.24	2.229	2.078	2.216	2.2069	2.092
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.006	0.043	0.016	0.0137	0.035
Mg	0.37	0.37	0.35	0.37	0.38	0.08	0.00	0.37	0.706	0.733	0.727	0.7172	0.770
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.037	0.138	0.026	0.0503	0.083
Na	0.00	0.00	0.00	0.06	0.08	0.27	0.91	0.00	0.00	0.00	0.00	0.00	0.00
K	0.86	0.88	0.86	0.86	0.79	0.68	0.03	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.80	0.80	0.82	0.79	0.79	0.49	0.00	0.12	0.24	0.25	0.24	0.24	0.26
XFe								0.75	0.75	0.69	0.74	0.74	0.70
XCu								0.05	0.01	0.05	0.01	0.02	0.03
XMn								0.07	0.00	0.01	0.01	0.01	0.01

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 11 oxygens for white mica and 12 oxygens for garnet.

Fe<sup>3+</sup> has been calculated by stoichiometry



**Table SM4b - Representative analyses of the main minerals in sample DM1281 (BIU)**

Analysis Site	Chloritoid				Chlorite		Staurolite	
	5.7 Cld* In Grt <sub>M</sub>	6.49 Cld* In Grt <sub>M</sub>	6.36 Cld* In Grt <sub>M</sub>	6.33 Cld* In Grt <sub>M</sub>	6.52 Chl In Grt <sub>C</sub>	10.24 Chl late	6b.5 St In Grt <sub>C</sub>	11.26 St In Grt <sub>C</sub>
SiO <sub>2</sub>	25.88	25.58	25.75	25.54	27.56	24.03	30.70	29.57
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
Al <sub>2</sub> O <sub>3</sub>	41.99	41.84	41.94	41.35	22.34	22.89	57.68	55.21
FeO	20.36	21.29	20.79	21.25	18.58	32.13	9.36	10.64
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	5.24	5.07	5.12	4.89	20.06	9.64	1.11	1.75
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	93.47	93.78	93.60	93.02	88.54	88.70	98.85	97.52
Si	2.07	2.04	2.06	2.06	2.77	2.61	4.26	4.17
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
Al	3.95	3.94	3.95	3.92	2.65	2.92	9.43	9.17
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe <sup>+2</sup>	1.36	1.42	1.39	1.43	1.56	2.91	1.09	1.25
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.62	0.60	0.61	0.59	3.01	1.56	0.23	0.37
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.31	0.30	0.31	0.29	0.66	0.35	0.18	0.23

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 14 oxygens for chloritoid, 18 oxygens for chlorite and 12 oxygens for staurolite.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM5a - Representative analyses of the main minerals in sample DM1504 (RSU)**

Analysis Site	White mica						Garnet					
	2.34 Phe*	6.21 Phe*	6.16 Phe*	6.3 Phe*	7.20 Ms	6.15 Pa	2.16 Grt	2.8 Grt	2.2 Grt*	2.26 Grt*	1.19 Grt*	2.1 Grt*
	In Grt <sub>R</sub>	// S <sub>m</sub>	// S <sub>m</sub>	In Cld	late	⊥ S <sub>m</sub>	Core	Mantle	Rim	Rim	Rim	Rim
SiO <sub>2</sub>	51.86	52.08	51.42	52.38	47.24	48.40	37.09	37.09	37.47	36.88	37.19	37.21
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	27.60	27.64	27.34	27.47	35.02	39.39	20.78	20.52	20.39	20.48	20.87	20.40
FeO	3.79	3.66	4.31	3.85	2.85	0.65	30.05	29.49	30.70	31.04	29.44	31.13
MnO	0.00	0.00	0.00	0.00	0.00	0.00	3.99	2.91	1.66	1.83	2.79	1.72
MgO	3.01	3.01	3.05	3.19	0.67	0.00	2.09	2.30	2.14	2.37	2.35	2.21
CaO	0.00	0.00	0.00	0.00	0.00	0.00	5.63	7.15	7.13	6.39	7.19	6.54
Na <sub>2</sub> O	0.58	0.00	0.78	0.72	1.92	7.68	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	9.75	10.35	9.46	9.32	8.33	0.24	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.59	96.74	96.36	96.93	96.02	96.37	99.63	99.46	99.50	98.99	99.83	99.22
Si	3.42	3.43	3.41	3.43	3.11	3.06	2.99	2.98	3.02	2.98	2.98	3.01
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	2.14	2.14	2.13	2.12	2.72	2.94	1.97	1.94	1.93	1.95	1.97	1.94
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.09	0.04	0.08	0.08	0.05
Fe <sup>+2</sup>	0.21	0.20	0.24	0.21	0.16	0.03	1.98	1.89	2.03	2.02	1.89	2.05
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.20	0.11	0.13	0.19	0.12
Mg	0.30	0.29	0.30	0.31	0.07	0.00	0.25	0.28	0.26	0.29	0.28	0.27
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.62	0.62	0.55	0.62	0.57
Na	0.07	0.00	0.10	0.09	0.25	0.94	0.00	0.00	0.00	0.00	0.00	0.00
K	0.82	0.87	0.80	0.78	0.70	0.02						
XMg	0.59	0.59	0.56	0.60	0.295	0.00	0.08	0.09	0.09	0.10	0.09	0.09
XFe							0.66	0.64	0.67	0.68	0.64	0.68
XCa							0.16	0.21	0.20	0.19	0.21	0.19
XMn							0.09	0.07	0.04	0.04	0.06	0.04

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 11 oxygens for white mica and 12 oxygens for garnet.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM5b - Representative analyses of the main minerals in sample DM1504 (RSU)**

Analysis	Chloritoid							Jadeite	Glaucophane
	7.9 Cld	1.22 Cld	1.20 Cld	6.8 Cld*	2.35 Cld*	4.4 Cld*	2.32 Cld*	2.44 Jd*	2.52 Gln*
Site	Core	In Grt <sub>C</sub>	In Grt <sub>M</sub>	Rim	In Grt <sub>R</sub>	In Grt <sub>R</sub>	In Grt <sub>R</sub>	In Grt <sub>R</sub>	In Grt <sub>R</sub>
SiO <sub>2</sub>	25.22	25.22	25.11	25.18	25.14	24.77	24.58	56.79	55.54
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	40.44	40.63	40.61	40.21	40.66	40.29	39.98	17.49	9.58
FeO	24.17	23.91	23.74	23.86	23.60	23.61	23.43	8.69	18.07
MnO	0.54	0.00	0.46	0.00	0.00	0.42	0.42	0.00	0.00
MgO	3.25	3.61	3.80	4.07	3.69	3.84	3.81	0.00	7.34
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.76
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.62	6.53
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	93.62	93.38	93.72	93.32	93.09	92.93	92.22	98.06	97.83
Si	2.05	2.05	2.03	2.04	2.05	2.02	2.05	2.00	7.83
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	3.87	3.89	3.87	3.85	3.90	3.87	3.87	0.73	1.59
Fe <sup>+3</sup>	0.02	0.01	0.06	0.07	0.01	0.09	0.04	0.26	0.53
Fe <sup>+2</sup>	1.62	1.61	1.54	1.55	1.60	1.52	1.56	0.00	1.60
Mn	0.04	0.00	0.03	0.00	0.00	0.03	0.03	0.00	0.00
Mg	0.39	0.44	0.46	0.49	0.45	0.47	0.46	0.00	1.54
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.11
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.79
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.20	0.21	0.23	0.23	0.22	0.23	0.23	0.00	0.48
XNa								0.98	0.94

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 14 oxygens for chloritoid, 6 oxygens for jadeite and 24 oxygens for glaucophane.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM6a - Representative analyses of the main minerals in sample DM1565 (DSU)**

Analysis Site	White mica						Pre-Alpine Garnet (Grt <sub>1</sub> )			Alpine Garnet (Grt <sub>2</sub> )			
	5.12 Phe*	5.6 Phe*	3.6 Phe*	2.27 Phe	8.18 Ms	5.3 Pa	1.16 Grt	t 1.6 Grt	1.30 Grt	3.13 Grt	3.15 Grt*	3.11 Grt*	7.1 Grt*
	// S <sub>m</sub>	// S <sub>m</sub>	// S <sub>m</sub>	ln (St)	Late	Late	Core	Mantle	Rim	Core	Rim	Rim	Rim
SiO <sub>2</sub>	54.76	54.59	55.21	51.93	47.53	47.68	36.89	36.86	36.61	37.28	37.58	37.53	37.37
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	25.84	25.43	25.42	28.58	37.05	40.10	21.05	20.54	20.64	20.98	21.08	20.93	21.39
FeO	2.57	2.20	2.72	2.77	0.94	0.00	34.38	35.62	35.81	34.17	31.62	29.92	30.68
MnO	0.00	0.00	0.00	0.00	0.00	0.00	2.68	0.65	1.92	1.07	0.75	0.81	0.78
MgO	4.20	4.34	4.17	3.02	0.55	0.00	1.94	2.33	2.66	0.95	1.37	1.11	1.13
CaO	0.00	0.00	0.00	0.00	0.00	0.00	2.77	3.24	1.46	5.30	7.09	9.11	8.59
Na <sub>2</sub> O	0.00	0.50	0.00	0.59	2.33	8.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	9.41	9.78	9.19	9.53	7.76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.78	96.85	96.71	96.42	96.84	96.18	99.71	99.24	99.10	99.75	99.48	99.42	99.93
Si	3.55	3.55	3.58	3.40	3.07	3.01	2.99	3.00	2.99	3.03	3.03	3.02	3.00
Ti	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	1.97	1.95	1.94	2.21	2.82	2.98	2.01	1.97	1.99	2.01	2.00	1.99	2.02
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.04	0.00	0.00	0.00	0.00
Fe <sup>+2</sup>	0.14	0.12	0.15	0.15	0.05	0.00	2.33	2.39	2.40	2.32	2.13	2.02	2.06
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.05	0.13	0.07	0.05	0.06	0.05
Mg	0.41	0.42	0.40	0.30	0.05	0.00	0.23	0.28	0.32	0.11	0.16	0.13	0.13
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.28	0.13	0.46	0.61	0.79	0.74
Na	0.00	0.06	0.00	0.07	0.29	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.78	0.81	0.76	0.80	0.64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XMg	0.744	0.778	0.732	0.66	0.511	0.00	0.08	0.09	0.11	0.04	0.06	0.05	0.05
XFe							0.78	0.80	0.80	0.78	0.72	0.67	0.69
XCa							0.08	0.09	0.04	0.16	0.21	0.26	0.25
XMn							0.06	0.02	0.04	0.03	0.02	0.02	0.02

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 11 oxygens for white mica and 12 oxygens for garnet.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM6b - Representative analyses of the main minerals in sample DM1565 (DSU)**

Analysis Site	Chloritoid			Chlorite
	2.3 Cld*	2.32 Cld**	2.25 Cld	8.14 Chl
	ln (St)	ln (St)	ln (St)	Late
SiO <sub>2</sub>	25.07	24.94	25.16	24.97
TiO <sub>2</sub>	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	41.12	41.39	40.95	21.77
FeO	24.15	24.13	25.23	29.31
MnO	0.00	0.00	0.00	0.00
MgO	2.80	2.89	2.52	11.99
CaO	0.00	0.00	0.00	0.00
Na <sub>2</sub> O	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.00	0.00	0.00
Total	93.14	93.35	93.87	88.04
Si	2.049	2.032	2.048	2.685
Ti	0.00	0.00	0.00	0.00
Al	3.959	3.974	3.928	2.758
Fe <sup>+3</sup>	0.00	0.00	0.00	0.00
Fe <sup>+2</sup>	1.650	1.644	1.718	2.636
Mn	0.00	0.00	0.00	0.00
Mg	0.342	0.350	0.306	1.922
Ca	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00
XMg	0.17	0.18	0.15	0.42

\* Analysis used for AvPT calculations (see Table 2)

Structural formulae have been calculated on the basis of 14 oxygens for chloritoid and 18 oxygens for chlorite.

Fe<sup>3+</sup> has been calculated by stoichiometry

**Table SM7a. Independent set of reactions modelled by AvPT and used to estimate P-T conditions**

<b>Sample DM1485 (PU)</b>	
Phe(6.1)-Grt(1.22)-Ctd(1.49)-Chl(4.7)-Qz-H <sub>2</sub> O	Phe(2.31)-Grt(1.2)-Ctd(1.48)-Chl(4.8)-Qz-H <sub>2</sub> O
1) ames + 2q = py + mctd + 3H <sub>2</sub> O	1) ames + 2q = py + mctd + 3H <sub>2</sub> O
2) 5alm + 5ames + 4q = 4py + 8mctd + 3daph	2) fctd + daph + 2q = 2alm + 5H <sub>2</sub> O
3) 23alm + 15ames + 12q = 20py + 24fctd + 9daph	3) 5alm + 5ames + 4q = 4py + 8mctd + 3daph
4) 3cel + 5alm + 3ames = 3mu + 5py + 3daph	4) 3cel + 5alm + 3ames = 3mu + 5py + 3daph
Phe(6.11)-Grt(1.21)-Ctd(2.29)-Chl(4.9)-Qz-H <sub>2</sub> O	Phe(6.6)-Grt(1.23)-Ctd(1.33)-Chl(3.7)-Qz-H <sub>2</sub> O
1) ames + 2q = py + mctd + 3H <sub>2</sub> O	1) ames + 2q = py + mctd + 3H <sub>2</sub> O
2) fctd + daph + 2q = 2alm + 5H <sub>2</sub> O	2) fctd + daph + 2q = 2alm + 5H <sub>2</sub> O
3) 5alm + 5ames + 4q = 4py + 8mctd + 3daph	3) 3mctd + 3daph + 6q = py + 5alm + 15H <sub>2</sub> O
4) 3mu + py + 2ames + 4q = 3cel + 8mctd	4) 3mu + py + 2ames + 4q = 3cel + 8mctd
5) 3cel + alm = 3fcel + py	5) 3cel + alm = 3fcel + py
<b>Sample DM1667c (SCU)</b>	
Phe(7.17)-Grt(2.24)-Ctd(1.5)-Lws-Qz-H <sub>2</sub> O	Phe(10.1)-Grt(9.22)-Ctd(2.52)-Lws-Qz-H <sub>2</sub> O
1) py + 3law = gr + 3mctd + 3q + 3H <sub>2</sub> O	1) py + 3law = gr + 3mctd + 3q + 3H <sub>2</sub> O
2) alm + 3law = gr + 3fctd + 3q + 3H <sub>2</sub> O	2) alm + 3law = gr + 3fctd + 3q + 3H <sub>2</sub> O
3) fcel + 2fctd = mu + alm + 2H <sub>2</sub> O	3) 3cel + 2gr + 12mctd + 6q = 3mu + 5py + 6law
4) 3cel + 2gr + 12mctd + 6q = 3mu + 5py + 6law	4) 15cel + 2gr + 12fctd + 6q = 3mu + 12fcel + 5py + 6law
Phe(10.9)-Grt(2.25)-Ctd(2.49)-Lws-Qz-H <sub>2</sub> O	Phe(1.18)-Grt(9.1)-Ctd(2.40)-Lws-Qz-H <sub>2</sub> O
1) py + 3law = gr + 3mctd + 3q + 3H <sub>2</sub> O	1) py + 3law = gr + 3mctd + 3q + 3H <sub>2</sub> O
2) alm + 3law = gr + 3fctd + 3q + 3H <sub>2</sub> O	2) alm + 3law = gr + 3fctd + 3q + 3H <sub>2</sub> O
3) 3cel + 2gr + 12mctd + 6q = 3mu + 5py + 6law	3) 3cel + 2gr + 12mctd + 6q = 3mu + 5py + 6law
<b>Sample DM1281 (BIU)</b>	
Phe(12.2)-Grt(6.3)-Ctd(5.7)-Ky-Coe-H <sub>2</sub> O	Phe(12.1)-Grt(6b.1)-Ctd(6.49)-Ky-Coe-H <sub>2</sub> O
1) 3fctd + 2co = alm + 2ky + 3H <sub>2</sub> O	1) 3fctd + 2co = alm + 2ky + 3H <sub>2</sub> O
2) 3mu + py + 4co = 3cel + 4ky	2) 3mu + py + 4co = 3cel + 4ky
3) 3cel + alm = 3fcel + py	3) 3cel + alm = 3fcel + py
Phe(6.88)-Grt(6.32)-Ctd(6.36)-Ky-Coe-H <sub>2</sub> O	Phe(8.3)-Grt(10.13)-Ctd(6.33)-Ky-Coe-H <sub>2</sub> O
1) 3fctd + 2co = alm + 2ky + 3H <sub>2</sub> O	1) 3fctd + 2co = alm + 2ky + 3H <sub>2</sub> O
2) 3mu + py + 4co = 3cel + 4ky	2) pa = ky + jd + H <sub>2</sub> O
3) 3cel + alm = 3fcel + py	3) 3mu + py + 4co = 3cel + 4ky
	4) 3cel + alm = 3fcel + py

**Table SM7b. Independent set of reactions modelled by AvPT and used to estimate P-T conditions**

<b>Sample DM1504 (RSU)</b>	
Phe(2.34)-Grt(2.2)-Ctd(2.35)-Gln(2.52)-Jd(2.44)-Lws-Qz-H <sub>2</sub> O	Phe(6.21)-Grt(2.26)-Ctd(4.4)-Gln(2.52)-Jd(2.44)-Lws-Qz-H <sub>2</sub> O
1) $py + 3law = gr + 3mctd + 3q + 3H_2O$	1) $py + 3law = gr + 3mctd + 3q + 3H_2O$
2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$	2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$
3) $cel + 2mctd = mu + py + 2H_2O$	3) $cel + 2mctd = mu + py + 2H_2O$
4) $3mctd + 2jd + 2q = 2pa + py + H_2O$	4) $fcel + 2fctd = mu + alm + 2H_2O$
5) $fcel + 2fctd = mu + alm + 2H_2O$	5) $12fcel + py + 4mctd + 8jd + 4q = 5mu + 7cel + 4fgl$
6) $3pa + fgl = 3fctd + 5jd + 4q + H_2O$	
7) $27mu + 9cel + 4spss + 12fgl + 12law = 36fcel + 24pa + 3py + 4gr + 12mnctd$	
Phe(6.16)-Grt(1.19)-Ctd(6.8)-Gln(2.52)-Jd(2.44)-Lws-Qz-H <sub>2</sub> O	Phe(6.3)-Grt(2.1)-Ctd(2.32)-Gln(2.52)-Jd(2.44)-Lws-Qz-H <sub>2</sub> O
1) $py + 3law = gr + 3mctd + 3q + 3H_2O$	1) $py + 3law = gr + 3mctd + 3q + 3H_2O$
2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$	2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$
3) $cel + 2mctd = mu + py + 2H_2O$	3) $cel + 2mctd = mu + py + 2H_2O$
4) $3mctd + 2jd + 2q = 2pa + py + H_2O$	4) $3mctd + 2jd + 2q = 2pa + py + H_2O$
5) $fcel + 2fctd = mu + alm + 2H_2O$	5) $fcel + 2fctd = mu + alm + 2H_2O$
6) $6fcel + 2pa + py + 2jd = 3mu + 3cel + 2fgl$	6) $3pa + fgl = 3fctd + 5jd + 4q + H_2O$
	7) $6fcel + 2pa + py + gr + 2acm = 3mu + 3cel + andr + 2fgl$
<b>Sample DM1565 (DSU)</b>	
Phe(5.12)-Grt(3.15)-Ctd(2.3)-Lws-Qz-H <sub>2</sub> O	Phe(5.6)-Grt(3.11)-Ctd(2.32)-Lws-Qz-H <sub>2</sub> O
1) $py + 3law = gr + 3mctd + 3q + 3H_2O$	1) $py + 3law = gr + 3mctd + 3q + 3H_2O$
2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$	2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$
3) $3cel + 2gr + 12mctd + 6q = 3mu + 5py + 6law$	3) $3cel + 2gr + 12fctd + 6q = 3mu + py + 4alm + 6law$
Phe(3.6)-Grt(7.1)-Ctd(2.25)-Lws-Qz-H <sub>2</sub> O	
1) $py + 3law = gr + 3mctd + 3q + 3H_2O$	
2) $alm + 3law = gr + 3fctd + 3q + 3H_2O$	
3) $3cel + 2gr + 12mctd + 6q = 3mu + 5py + 6law$	

**Table SM8 - Mass balance of the staurolite-forming reactions**

**0.264 Chl + 3.496 Ky + 0.123 Grt<sub>c</sub> = 1.000 St**

	Reactants			Products			
Phases	Chl 6.68	Ky 6.66	Grt <sub>c</sub> 6.15	St 6.67	Σ <sub>react</sub>	Σ <sub>prod</sub>	Residuals
<b>coeff</b>	<b>-0.264</b>	<b>3.496</b>	<b>-0.123</b>	<b>1.000</b>			
SiO <sub>2</sub>	2.59	1.00	2.98	3.94	-3.940	4.544	0.604
Al <sub>2</sub> O <sub>3</sub>	1.47	1.00	1.00	4.61	-4.610	4.006	-0.604
FeO	2.48	0.00	2.30	1.51	-1.510	0.936	-0.574
MnO	0.00	0.00	0.10	0.00	0.000	0.012	0.012
MgO	1.93	0.00	0.45	0.29	-0.290	0.564	0.274
CaO	0.00	0.00	0.14	0.01	-0.008	0.018	0.010
H <sub>2</sub> O	4.00	0.00	0.00	1.00	-1.000	1.055	0.055

**0.263 Chl + 3.712 Ky + 0.064 Grt<sub>c</sub> = 1.000 St**

	Reactants			Products			
Phases	Chl 11.34	Ky 11.32	Grt <sub>c</sub> 11.6	St 11.34	Σ <sub>react</sub>	Σ <sub>prod</sub>	Residuals
<b>coeff</b>	<b>-0.263</b>	<b>-3.712</b>	<b>-0.064</b>	<b>1.000</b>			
SiO <sub>2</sub>	2.71	1.00	2.90	4.11	-4.110	4.610	0.500
Al <sub>2</sub> O <sub>3</sub>	1.56	1.00	1.00	4.69	-4.685	4.185	-0.500
FeO	2.43	0.00	2.19	1.27	-1.270	0.779	-0.491
MnO	0.00	0.00	0.10	0.00	0.000	0.006	0.006
MgO	1.75	0.00	0.54	0.26	-0.260	0.494	0.234
CaO	0.00	0.00	0.16	0.00	0.000	0.010	0.010
H <sub>2</sub> O	4.00	0.00	0.00	1.00	-1.000	1.052	0.052

**0.211 Chl + 3.620 Ky + 0.131 Grt<sub>M</sub> = 1.000 St**

	Reactants			Products			
Phases	Chl 6.52	Ky 6.53	Grt <sub>M</sub> 6.21	St 6.50	Σ <sub>react</sub>	Σ <sub>prod</sub>	Residuals
<b>coeff</b>	<b>-0.211</b>	<b>-3.620</b>	<b>-0.131</b>	<b>1.000</b>			
SiO <sub>2</sub>	2.77	1.00	2.99	4.04	-4.040	4.598	0.558
Al <sub>2</sub> O <sub>3</sub>	1.33	1.00	1.00	4.59	-4.590	4.032	-0.558
FeO	1.56	0.00	2.05	1.23	-1.230	0.599	-0.631
MnO	0.00	0.00	0.08	0.00	0.000	0.010	0.010
MgO	3.01	0.00	0.67	0.46	-0.460	0.724	0.264
CaO	0.00	0.00	0.17	0.00	0.000	0.022	0.022
H <sub>2</sub> O	4.00	0.00	0.00	1.00	-1.000	0.846	-0.154

Reactions were balanced using the least-squares method. Stoichiometric coefficients and compositions are expressed in moles. *Σ<sub>react</sub>*: overall composition of the reactants; *Σ<sub>prod</sub>*: overall composition of the products; *Residuals*: residual vector from the method of least squares (molar bulk composition of the product - molar bulk composition of the reactants).